

✓ **EFFECT OF CATALYST ACTIVITY DISTRIBUTION ON
ACTIVITY AND SELECTIVITY ON AMPHORA CATALYST**

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In Partial Fulfilment of the Requirements
for the Degree of
MASTER OF TECHNOLOGY

By
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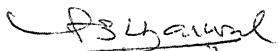
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CERTIFICATE

This is to certify that the present work 'EFFECT OF CATALYST ACTIVITY DISTRIBUTION ON ACTIVITY AND SELECTIVITY ON AMPHORA CATALYST' has been carried out under my supervision and has not been submitted elsewhere for a degree.

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YAQOOB ALI

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ABSTRACT

An amphora catalyst which resembles a hollow sphere with two openings, on the two sides, has been chosen for study. The active catalyst is dispersed nonuniformly over amphora. Two types of distribution have been studied, the first one is non-uniform distribution with α , as activity distribution parameter whose value has been changed from 0 to 8 and the second one Dirac-delta type distribution.

It has been found that amphora catalyst with uniform activity distribution ($\alpha=0$) gives better effectiveness factor and selectivity over conventional spherical catalyst. When the value of α is increased to 1 (linear distribution), or to 2 (parabolic distribution) or more than 2, the activity and selectivity is found to increase.

For Dirac-delta distribution, generalised optimal location has been defined and it is shown that as the Thiele parameter increases, the optimal location shifts towards the surface of the pellet and at very high values of Thiele parameter, the optimal strategy is to apply all the active material on the surface.

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NOMENCLATURE

| | |
|------------------------|---|
| a | Boundary value at the inner surface. |
| a_0 | Volume averaged catalyst density. |
| $a(z)$ | Local catalyst density. |
| b | Boundary value at the outer surface. |
| C_1, C_2 | Concentration of components A and B respectively. |
| C_{10}, C_{20} | Surface concentration of components A and B, respectively. |
| De_1, De_2 | Effective diffusivities of components A and B respectively. |
| F | A vector containing the boundary values at external surface. |
| G | A function of u_1 . |
| h | Step width. |
| K_1, K_2 | Local rate constant for first and second reactions. |
| \bar{K}_1, \bar{K}_2 | Average rate constant for first and second reactions. |
| n, N | Number of difference points. |
| r, R | Radius of the pellet |
| \bar{S} | Global selectivity. |
| u, u_1, u_2 | Dimensionless concentration of A and B respectively. |
| u_2^0 | Initial surface concentration of component B. |
| u_3, u_4 | Dimensionless concentration gradient of components A and B respectively. |
| $u_{1,c}, u_{2,c}$ | Concentration of component A and B respectively where the active catalyst is applied. |
| $u_{1,opt}$ | Optimal concentration of component A. |
| dV_p | Volume element. |
| V | Volume of the pellet. |

| | |
|------------------------------|---|
| \vec{V} | Vector containing boundary values. |
| Y | Yield of the desired product. |
| z | Dimensionless radius. |
| z_c | Distance at which the active catalyst is applied. |
| z_{opt} | Optimal distance where the active catalyst is applied. |
| α | Activity distribution parameter. |
| β | Width of the step distribution. |
| δ | Dirac-delta distribution. |
| $\delta_{ext}, \delta_{int}$ | Optimized parameters for external and internal surfaces . |
| ξ | Ratio of diffusion coefficients |
| ϕ_1, ϕ_2 | Thiele parameter for first and second reactions. |
| Θ | Jacobian. |
| σ | Characteristic length. |
| μ | Optimization parameter. |
| Δ | Width of step distribution. |
| λ | Ratio of the kinetic constants. |

CHAPTER 1

INTRODUCTION

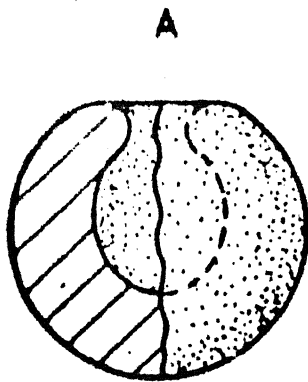
Mass and heat transfer limitations are often important considerations in heterogeneous catalysis. Chemical reactions that are diffusion limited are being greatly benefited from the use of smaller catalyst particles, because of their smaller internal diffusional path length. By minimizing residence time of product molecules within the catalyst particles, secondary reactions can be minimized and selectivity can be increased.

Keeping in view, the higher surface to volume ratio, the researchers have introduced a variety of catalyst shapes over the years. Spherical catalysts have been used in place of extrudates or tablets because of their higher surface to volume ratio and better packing efficiency.

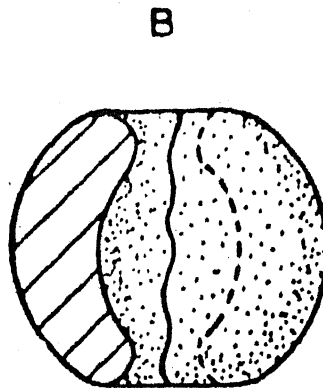
THE AMPHORA

In the late 1950's Sohio research laboratory was busily expanding its acrylonitrile technology, in course of developing a spray drying process for making fluid bed catalyst (17).

Jim Callahan made an interesting discovery, upon viewing a sample of spray dried catalyst under the microscope. He found that a number of particles had an unexpected shape. Scattered among the spheres were particles that had channels



Amphora I



Amphora II

Fig. 1A Cross-sectional drawing of a representative particle amphora I

Fig. 1B Cross-sectional drawing of a representative particle amphora II

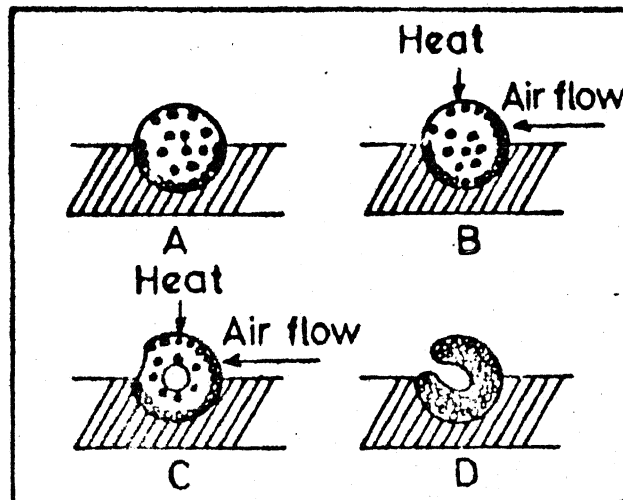


Fig. 2 -Mechanism of amphora formation.

leading from the outside to the hollow centre. These new particles, if they can be produced in sizes appropriate for fixed-bed applications, would offer a unique combination of advantages. The new shapes have a higher surface to volume ratio, than solid spheres. Most importantly, if the inner cavity would be made to be half the diameter of the particle, the effective particle thickness would be 1/4th that of the particle diameter. Thus a bed of 3 mm diameter particles would have the performance characteristics of 0.75 mm solid sphere, Fig. (1).

Name for the new particle shape, again, was suggested by Callahan. He called them Amphorae, for the ancient Greek urns that were used to carry cargo on trading ships. The Greek amphorae were shaped so that they stacked uniformly and efficiently in the ships holds, and therein lies the analogy. The industrial process of making amphora was described by Harrington (17).

MECHANISM OF AMPHORA FORMATION

The actual mechanism for amphora formation, developed by G.K. Meloy, is a variation of one of the classic mechanism of the drying of a sphere in spray drying processes. In that mechanism a rigid shell is initially formed on the surface of the sphere so that further drying occurs by migration, solid particles are carried with the liquid. Because the rate of liquid migration and evaporation is faster than the rate of diffusion of the solid particles back into the interior, a hollow sphere is formed.

Meloy found that the variation of this mechanism that results in amphora formation is one of unequal evaporation rates over the surface of the spherical particle. This is attained by a unidirectional air flow over slurry droplets as they are drying. The air flow speeds evaporation on one side of the exposed portion of the droplet, rigidizing that portion but leaving an area of greater fluidity on the other-side of the droplet capable of plastic flow. As drying continues and natural shrinkage occurs, the particle first forms a hollow centre and then, to relieve surface stresses and minimize surface energy, the area of greater fluidity shrinks into the particle and the hole is pulled. Fig.(2).

Experiments carried out at Sohio (17) proved that amphora catalysts could indeed outperform conventionally shaped catalysts in reactions limited by heat and / or mass transfer. The tables 1, 2, 3, compare the amphora and other conventional catalysts.

INTRODUCTION TO NON UNIFORMLY ACTIVE CATALYST

An extensive literature exists dealing with the interactions between the physical and chemical transport phenomena of the heterogeneous catalysis and the distribution of catalytically active material within the particles assumed to be uniform (3,4,31,44,45). The effects of intraparticle mass and heat diffusional resistances in catalysts exhibiting uniform activity distributions have been extensively studied by these workers in terms of point and overall effectiveness,

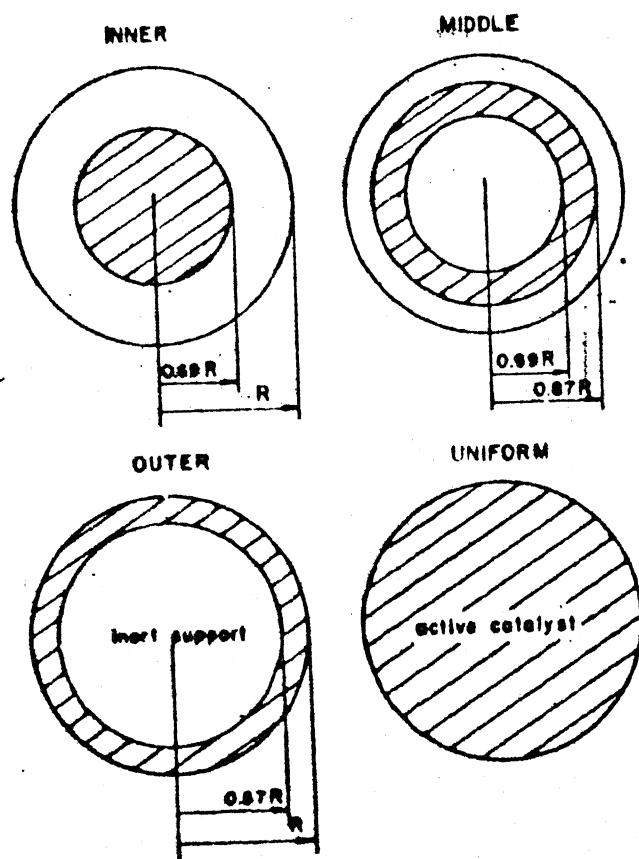


Fig. 3 - Various types of distributions.

selectivity, yield and the concentrations and temperature profiles, within a single particle (34) and in the chemical reactors.

Kasaoka and Sakata (22) first studied the non uniform catalytic effectiveness factor with variable rate constants and diffusivities theoretically on flat pellets. Corbett and Luss (8) have shown the effect of non uniform activity distribution of a single spherical pellet on its effectiveness factor, selectivity and deactivation . In most cases the performance of nonuniformly active catalysts is superior to that of uniformly active catalysts which have the same volume averaged activity. The specific deactivation mechanisms and rate as well as diffusional resistance have an important influence on the most desired activity profile.

Bimolecular Langmuir kinetics under isothermal conditions, was studied by Becker and Wei (5) and shown that the 'egg yolk' type distribution gives the greater activity than that the traditional egg shell or uniform distribution Fig. (3). The optimal activity distribution inside the isothermal and nonisothermal pellets of spherical, cylindrical and slab geometries with negligible and considerable external mass transfer resistance under steady state conditions was studied by Morbidelli et.al (24,25), Juang (19) Ready Karri (30), Gottifredi (14), Shadman-Yazdi (32), and Vayenas and Pavlov (35,36, 37). These researchers concluded that the optimum distribution is the approximately chosen Dirac $-\delta$ type distribution and they generalized the optimum distance for varying conditions, giving

the maximum effectiveness factor, selectivity, yield and durability of the catalysts. Analytical expressions for this location as the function of all the involved physiochemical parameters are given in three pellet geometries by Vayenas and Pavlov (35,36,37). Numerical computations are reported by Morbidelli, Servida (24) to analyze the case where the active catalyst is deposited in a step manner centered around the optimal location.

Same results were obtained by Morbidelli (27) with reference to the synthesis of ethylene oxide. The most suitable objective function has been proposed and a very easy optimization technique, which identifies a close approximation of the optimal radial activity distribution, has been developed. This leads to a Dirac delta function in practice approximated by a step distribution whose width is about 4% of the particle radius, centered at a particular radial location within the particle, which depends upon the operating conditions.

Johnson and Verykios (20) studied theoretically the selectivity enhancement in ethylene oxidation employing partially impregnated catalyst, using the experimental data and reported the effects of radially nonuniform distributions of catalytic activity on the performance of spherical catalyst pellets under ethylene oxidation. They also showed that partially impregnated catalyst exhibits higher activity and selectivity at higher value of Thiele modulus, than the uniformly active catalyst pellets. They also observed the multiple steady state effectiveness factor

and selectivity under sufficiently high values of the heat of reaction parameter.

Simultaneous, bimolecular, complex reactions, and Michaelis -Menton kinetics under exothermic conditions was studied by Johnson and Verykios (21) and Cukierman et.al (9), Horvath (18) . They assumed the distribution function of the form: $k(r) = k_s(r/r_s)^\alpha$, $\alpha > 0$ and the reactions were assumed to be of the second order. Effectiveness factor and overall pellet selectivities for various values of the dimensionless activation energies and heat of reaction parameter were reported as a function of the thiele modulus.

Analytical evaluation of the isothermal and non-isothermal fixed bed reactors were reported by Morbidelli and Verma (28,29), Smith (33), Juang and Weng (19), Cukierman et.al (9). They showed that the reactor can possess at most three steady states and that the issue of reactor multiplicity and stability is intimately tied up with multiplicity and stability for the first layer of pellets packed along the axial direction. The patterns of reactor behaviour, including ignition phenomena is fully characterized as a function of three dimensionless parameters viz, adsorption constant, β , which depends upon thiele parameter and the Damkohlar number.

For a bimolecular Langmuir-Hinshelwood kinetics, the rigorous optimal distribution is found to be a Dirac delta function centered at a location inside the pellet which depends on position along the reactor axis. They have also shown that

the nonuniformly active distribution also plays an important role in controlling the temperature profiles inside the reactor. Smith (33) reported that yield can be substantially improved by a step distribution.

Poisoning with shell progressive models, poremouth poisoning, activation policy for poisoning, parallel and series poisoning was studied by Vayenas (38), Ardiles (2), DeLancey (10) and Juang and Weng (19). Vayenas (38) reported that when the rate limiting step is the chemical reaction the optimal strategy is to concentrate the active component in a thin shell located inside a pellet. Thus the poisoning by shell progression can be avoided. The same results were reported by Ardiles. Juang and Weng shown that the convex and concave profiles may significantly resist the homogenous poisoning in the form of series and parallel fouling.

Shape normalization and the analytical expressions for the effectiveness factor and selectivity and their analytical solution were given by Yortsos and Tsotsis (42,43), Wang and Varma (39,40), Morbidelli and Varma (26). They developed the shape normalization technique for nonuniformly active catalyst pellets with an isothermal first order reaction. The shape normalized curves, obtained for different geometries, activity profiles and external mass transfer resistance match perfectly for small and/or large values of the thiele modulus. Yortsos and Tsotsis developed the shape normalization by using the Liouville-Green expression for asymptotic behaviour of the

effectiveness factor. They also reported that the normalization has no meaning when the surface catalytic activity is zero.

The optimization by very simple technique was done by Morbidelli (24,25), DeLancy (10). They employed the Pontryagin's continuous maximum principle to obtain the optimal profiles. Dougherty and Verykios (12) reproduced the various techniques of optimization and reported that approximately chosen Dirac delta is the best recommended profile.

Beyond the theoretical research impregnation models and experimental studies, on the nonuniformly active catalyst was done by Harriott (16), Minhas and Carberry (23), and Wu et.al (41). Wu, first time studied experimentally, the existence of the optimal active catalyst distribution, and the dependence of the effectiveness factor vs. thiele modulus in nonisothermal pellets. For the hydrogenation of ethylene on $\text{Pd}/\text{Al}_2\text{O}_3$ catalyst and the methanation of Co on $\text{Ni}/\text{Al}_2\text{O}_3$ catalyst, by use of step distribution with the active layer of narrow width to approximately replace the distribution of the Dirac delta type, it was shown that there did exist an optimal location of the active layer within the pellet at the given conditions and the optimal location moves towards the external surface as the thiele modulus increases.

In the present work we theoretically studied the active profiles in the new catalyst shape, called amphora.

We reported the effectiveness factor, selectivity and yield for the various type of distributions like uniform, linear, parabolic, hyperbolic and the Dirac delta. We have shown that the maximum selectivity and the effectiveness factor was obtained by the Dirac delta distribution, the site of which depends upon the operating conditions. It has, also been shown that at very low value of thiele modulus the whole thing should be centred in the pellet, and as the thiele modulus increases the optimal location moves towards the surface and thus when the reaction is highly diffusion controlled, i.e., when the thiele modulus is very high, the whole active sites should be applied on the surface. Which is properly known as the 'egg shell' type distribution.

A generalized activity distribution function, has also been defined by equation (25). Here the most important thing is that, since the amphora has the two surfaces, hence we need two type of profiles in the same pellet. And also in case of the Dirac delta type distribution there exist two optimal locations, which has been reported.

Table 1. Oxidation of propylene to acrolein/acrylic acid
(amphorae vs tableted catalyst)

| Catalyst form | Temperature (°C) | <u>Corrected % per pass conversion</u> | | | |
|---------------------------|---------------------|--|----------|--------------------------|----------|
| | | Acrylic Acid | Acrolein | Total Conver- sion | % Useful |
| 5mm X 2.8 mm Tablets | 310 | 4.8 | 74.8 | 81.7 | 79.6 |
| 5mm X 2.8 mm Tablets | 329 | 7.7 | 82.6 | 92.9 | 90.3 |
| 5mm X 2.8 mm Tablets | 338 | 8.8 | 82.0 | 93.6 | 90.8 |
| 3.1mm Diameter amphora | 310 | 7.1 | 84.3 | 93.9 | 91.4 |
| 3.1mm Diameter amphora | 327 | 10.8 | 83.1 | 96.8 | 93.9 |
| 3.1mm Diameter amphora | 338 | 13.1 | 82.6 | 99.5 | 95.7 |

Table 2. Oxidation of O-xylene to phthallic anhydride
(amphorae vs. solid spheres)

| Catalyst from | Temperature (°C) | Exotherm (°C) | Corrected % per pass Conversion | | |
|------------------|---------------------|------------------|---------------------------------|------|-----------------|
| | | | Phthallic anhydride | CO | CO ₂ |
| Amphora | 353 | 18 | 67.8 | 3.3 | 11.4 |
| Spherical | 348 | 20 | 71.2 | 7.3 | 21.5 |
| Amphora | 368 | 20 | 78.8 | 5.3 | 14.1 |
| Spherical | 361 | 26 | 63.8 | 9.5 | 26.7 |
| Amphora | 381 | 22 | 77.7 | 5.9 | 16.4 |
| Spherical | 376 | 40 | 53.3 | 12.9 | 33.9 |

Table 3. Oxydehydrogenation of 2-butene to butadiene (amphorae
vs. tablets)

| Catalyst form | Temperature (°C) | Butadiene | Maleic anhydride | Total conversion | % useful |
|------------------|---------------------|-----------|---------------------|---------------------|----------|
| Tablet | 302 | 40.4 | 1.1 | 44.5 | 41.5 |
| Amphora | 302 | 48.2 | 1.5 | 53.5 | 49.7 |
| Tablet | 329 | 69.5 | 3.4 | 78.5 | 72.9 |
| Amphora | 329 | 72.6 | 6.7 | 88.0 | 79.3 |

Reported from reference No. (17).

CHAPTER 2

FORMULATION OF THE PROBLEM

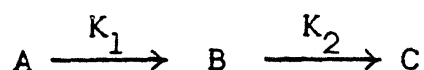
As it is seen the Amphora II catalyst Fig.(1) particles are spherical in shape and the most advisable ratio of inner to outer radius is $1/2$, as was suggested by Herrington (17). Amphora II has two naturally occurring openings on diametrically opposite points. Keeping these features in mind about the shape of the Amphora II, following assumptions are made in modelling of the non uniformly active catalyst for diffusion problems with negligible external phase mass transfer resistance:

1. The catalyst particle is spherical in shape with cavity inside.
2. There are two openings for fluid transportation to and from the inside surface.
3. Ratio of the external diameter to the internal diameter is 2.
4. The volume occupied by the openings is small as compared with the total volume of the particle. Thus the small material loss can be ignored.
5. The external phase mass transfer resistance, out side the external surface and in the cavity is negligible.

On the basis of the above assumptions the model reduces to the hollow sphere with ratio of outer to inner diameter being 2. And the boundary conditions, on the basis of the assumption 5, are reduced to the Dirichlet type.

CONSECUTIVE REACTIONS:

We consider the following first order, isothermal, consecutive reaction with negligible external phase mass transfer resistance.



Where K_1 and K_2 are the rate constants and B, the intermediate product, is the desired product also. The steady state mass balance equations for A and B follows from Aris (3),

$$De_1 \nabla^2 C_1 = K_1 C_1 a(r) \quad \dots\dots\dots (1)$$

$$De_2 \nabla^2 C_2 = (K_2 C_2 - K_1 C_1) a(r) \quad \dots\dots\dots (2)$$

Where C_1 and C_2 are the concentrations of components A and B respectively and $a(r)$ is the local active catalyst density, which is defined as

$$\int_{V_p} a(r) dv = a_o v_p \quad \dots\dots\dots (3)$$

Where a_o is the volume averaged active catalyst distribution inside the pellet and v_p is the total volume of the amphora pellet.

On the basis of the assumptions made in the beginning of this chapter, the boundary conditions, to solve the steady state mass balance equations (1) and (2) are given as

$$C_1 = C_{10} \text{ on surface} \quad \dots\dots\dots (4)$$

$$C_2 = C_{20} \text{ on surface} \quad \dots\dots\dots (5)$$

NONDIMENSIONALIZATION OF THE EQUATIONS:

We introduce the following nondimensional quantities to solve the equations (1) and (2) numerically.

$$\begin{aligned}
 z &= \frac{r}{R} \\
 u_1 &= \frac{C_1}{C_{10}}, \quad u_2 = \frac{C_2}{C_{10}} \\
 \phi_1^2 &= \frac{\bar{K}_1 \sigma^2}{De_1}, \quad \phi_2^2 = \frac{\bar{K}_2 \sigma^2}{De_2}
 \end{aligned}$$

$$\xi = \frac{De_1}{De_2}, \quad \sigma^2 = \frac{7}{24} R^2$$

$$K_1 = \bar{K}_1 a(r), \quad K_2 = \bar{K}_2 a(r)$$

$$u_2^0 = \frac{C_{20}}{C_{10}},$$

$$a(z) = \frac{a(r)}{a_0}$$

As the amphora II under certain simplified assumptions becomes the hollow sphere. Putting these dimensionless variables into equations 1 to 5 and expanding the equations (1) and (2) in the spherical geometry, we got the following dimensionless equations.

$$\frac{1}{z^2} \frac{d}{dz} \left(z^2 \frac{du_1}{dz} \right) = \phi_1^2 u_1 a(z) \quad \dots \quad (6)$$

$$\frac{1}{z^2} \frac{d}{dz} \left(z^2 \frac{du_2}{dz} \right) = \phi_2^2 u_2 a(z) - \xi \phi_1^2 u_1 a(z) \dots \quad (7)$$

and the boundary conditions reduces to,

$$u_1 = 1.0 \quad \text{on the surface} \quad \dots \quad (8)$$

$$u_2 = u_2^0 \quad \text{on the surface} \quad \dots \quad (9)$$

As was suggested by Herrington (17) that the most probable ratio of external to internal diameter is 2, so the equations (8) and (9) can be written in the more general form,

$$u_1(1) = u_1(0.5) = 1.0 \quad \dots\dots (10)$$

$$u_2(1) = u_2(0.5) = u_2^0 \quad \dots\dots (11)$$

Equation(3) can be reduced in the dimensionless form, and each type of profile should satisfy this equation,

$$\int_{0.5}^{1.0} a(z) z^2 dz = \frac{7}{24} \quad \dots\dots (12)$$

From equation (7) the nondimensionless rate of formation of component B, is given by,

$$\int_{0.5}^1 z^2 \frac{du_2}{dz} dz = \int_{0.5}^1 (\phi_2^2 u_2 - \epsilon \phi_1^2 u_1) a(z) z^2 dz \quad \dots(13)$$

It can be further simplified as ,

$$\left(\frac{du_2}{dz}\right)_{z=1} - 0.25 \left(\frac{du_1}{dz}\right)_{z=0.5} = \int_{0.5}^1 (\phi_2^2 u_2 - \epsilon \phi_1^2 u_1) a(z) z^2 dz \quad \dots(14)$$

But $\left(\frac{du_2}{dz}\right)_{z=1} = - \left(\frac{du_1}{dz}\right)_{0.5}$, since both are on the opposite directions and of course at the surfaces.

Hence equation (14) can be reduced

$$-\left(\frac{du_2}{dz}\right) = \frac{4}{5} \int_{0.5}^1 (\phi_1^2 u_1 - \phi_2^2 u_2) a(z) z^2 dz \quad \dots (15)$$

Similarly the dimensionless rate of consumption of component A is given by the following equation,

$$\left(\frac{du_1}{dz}\right) = \frac{4}{5} \int_{0.5}^1 \phi_1^2 u_1 a(z) z^2 dz \quad \dots (16)$$

Selectivity can be defined as the net rate of formation of the desired product to that of the rate of consumption of the key component. In the mathematical form, the global selectivity of this single pellet can be defined as,

$$\bar{S} = - \frac{De_2 \left(\frac{dC_2}{dr}\right) \text{ on surface}}{De_1 \left(\frac{dC_1}{dr}\right) \text{ on surface}} \quad \dots (17)$$

Making this equation dimensionless and putting the values of the derivatives from equations (15) and (16) we got the following relations,

$$\bar{S} = -\frac{1}{\xi} \frac{\left(\frac{du_2}{dz}\right) \text{ on surface}}{\left(\frac{du_1}{dz}\right) \text{ on surface}} \quad \dots (18)$$

Or,

$$\bar{S} = 1 - \frac{\frac{1}{\xi} \int_{0.5}^1 \phi_2^2 u_2 a(z) z^2 dz}{\int_{0.5}^1 \phi_1^2 u_1 a(z) z^2 dz} \quad \dots (19)$$

$$\text{put } \lambda = \frac{\phi_2^2}{\phi_1^2} \quad \dots (20)$$

We further reduce equation (19) as following

$$\bar{S} = 1.0 - \frac{\int_{0.5}^{1.0} u_2 a(z) z^2 dz}{\int_{0.5}^1 u_1 a(z) z^2 dz} \times \frac{\lambda}{\xi} \quad \dots (21)$$

The ratio of surface fluxes expressed as the selectivity \bar{S} will be negative when there is the net consumption of the desired product and positive when there is the net formation of this product.

The effectiveness factor of the component A is defined as ratio of the rate of diffusion effected reaction to that of diffusion free reaction. More mathematically this can be represented as,

$$\eta = \frac{\int_{0.5}^{1.0} u_1 a(z) z^2 dz}{\int_{0.5}^{1.0} a(z) z^2 dz} \quad \dots (22)$$

from the use of equation (12) and (16) the above relation can be reduced to,

$$\eta = \frac{24}{7} \times \frac{5}{4} \times \frac{1}{\phi_1^2} \left(\frac{du_1}{dz} \right) \quad \dots (23)$$

The yield is given by ,

$$Y = \eta \times \bar{S} \quad \dots (24)$$

Where Y is the yield of the desired product. The yield represents the actual amount of B formed and it may be possible to counteract low selectivity with high activity to maintain the yield.

The differential equations (6) and (7) were solved and it was found that at the dimensionless radius equal to 0.72 the flux becomes zero. Keeping this in view we define a general

function which satisfies equation (12). The function is given as,

$$\begin{aligned}
 a(z) &= \frac{19}{192} \times \frac{2^{3-\alpha} \times \left(\frac{4}{3}\right)^{3-\alpha}}{2^{3-\alpha} - \left(\frac{4}{3}\right)^{3-\alpha}} z^{-\alpha} (3-\alpha) && \text{when } z < 0.72 \\
 & && \dots (25) \\
 &= \frac{37}{192} \times \frac{\left(\frac{4}{3}\right)^{3+\alpha}}{\left(\frac{4}{3}\right)^{3+\alpha} - 1.0} z^{+\alpha} (\alpha+3) && \text{when } z \geq 0.72
 \end{aligned}$$

where $\alpha \geq 0$

When we change the values of alpha, we got the different type of distributions:

| | |
|--------------|----------------|
| $\alpha = 0$ | uniform |
| $\alpha = 1$ | linear |
| $\alpha = 2$ | parabolic etc. |

By using these expressions we solved the equations for various values of α and the results are given in chapter 4 and the method of solution is discussed in chapter 3.

DIRAC DELTA TYPE DISTRIBUTION:

After analysing the various distribution functions, now we will analyse the Dirac - delta type distribution. For

the Amphora II, we define the function which must satisfy the constant of equation (12):

$$a(z) = \frac{\partial(z-z_c)}{\frac{24}{7} z^2} \quad \dots (26)$$

Amphora shape has two surfaces, and the diffusion takes place from both the surfaces. Accordingly there will be two Dirac-delta functions, one for external surface and another for internal surface, satisfying the requirement of the characteristic equation (12):

Substituting equation (26) in equation (6) and (7) we get the following relations.

$$z^2 \frac{du_1}{dz} = \phi_1^2 u_{1,c} \quad \dots (27)$$

Or
$$\int_{z_c}^{1.0} du_1 = \phi_1^2 u_{1,c} \int_{z_{cext}}^{1.0} z^{-2} dz$$

$$1-u_{1,c} = \phi_1^2 u_{1,c} \mu_{ext} \quad \dots (28)$$

Where $u_{1,c}$ is the concentration of component A, where active sites are situated. And z_{cext} is the active catalyst location, and μ_{ext} is given by ,

$$\mu_{ext} = \int_{z_{cext}}^{1.0} z^{-2} dz \quad \dots (29)$$

and for the internal surface it becomes,

$$\mu_{int} = \int_{0.5}^{z_{cint}} z^{-2} dz \quad \dots (30)$$

Similarly equation (7) becomes .

$$1 - u_{2,c} = \mu_{\text{ext}} (\phi_2^2 u_{2,c} - \phi_1^2 u_{1,c}) \quad \dots\dots (31)$$

where $u_{2,c}$ is concentration of component B at the location where the active material is applied.

Now we put this Dirac-delta function in equation (21) and we get the global selectivity for this function,

$$\bar{S} = 1.0 - \left(\frac{\lambda}{\xi} \right) \frac{\int_{z_c}^{1.0} z^2 u_2 (\partial(z-z_c) / z^2) dz}{\int_{z_c}^{1.0} z^2 u_1 (\partial(z-z_c) / z^2) dz} \quad \dots\dots (32)$$

Or,

$$\bar{S} = 1.0 - \left(\frac{\lambda}{\xi} \right) \frac{u_{2,c}}{u_{1,c}} \quad \dots\dots (33)$$

And also the selectivity is defined by equation (18),

$$\bar{S} = - \left(\frac{1}{\xi} \right) \frac{(du_2/dz)}{(du_1/dz)} \quad \dots\dots (18)$$

equation (18) can be written as,

$$\bar{S} = - \left(\frac{1}{\xi} \right) \left(\frac{du_2}{du_1} \right) \quad \dots\dots (34)$$

putting the values of derivatives the above equation can be reduced,

$$\bar{S} = \left(\frac{1}{\xi} \right) \frac{u_{2,c} - u_2^0}{1.0 - u_{1,c}} \quad \dots\dots (35)$$

Equation (33) and (35) are the same, so equating these we have,

$$\bar{S} = \left(\frac{1}{\epsilon}\right) \frac{u_{2,c} - u_2^0}{1.0 - u_{1,c}} = 1.0 - \left(\frac{\lambda}{\epsilon}\right) \frac{u_{2,c}}{u_{1,c}} \quad \dots\dots (36)$$

Rearranging the above equation,

$$u_{2,c} = u_{1,c} \left(\frac{\epsilon - \epsilon u_{1,c} + 1.0}{\lambda - \lambda u_{1,c} - u_{1,c}} \right) \quad \dots\dots (37)$$

In the above relation we have written $u_{2,c}$ in terms of $u_{1,c}$. Thus a function G can be defined such as $u_{2,c} = G(u_{1,c})$

Hence,

$$G(u_{1,c}) = u_{1,c} \left(\frac{\epsilon - \epsilon u_{1,c} + 1.0}{\lambda - \lambda u_{1,c} - u_{1,c}} \right) \quad \dots\dots (38)$$

equation (34) can be rewritten in the form of function G . Thence the maximum selectivity is given by,

$$\bar{S}_{\max} = \frac{G(u_{1,\text{opt}}) - u_2^0}{(1 - u_{1,\text{opt}})} \quad \dots\dots (39)$$

or equivalently,

$$\bar{S}_{\max} = 1.0 - \left(\frac{\lambda}{\epsilon}\right) \frac{G(u_{1,\text{opt}})}{u_{1,\text{opt}}} \quad \dots\dots (40)$$

Where $u_{1,\text{opt}}$ is the $u_{1,c}$ value which maximizes the right hand sides of equation (39) and (40). From equations (36)-(40) we can determine the value of \bar{S}_{\max} and $u_{1,\text{opt}}$ graphically. The tangent gives the value of $u_{1,\text{opt}}$ at the particular operating conditions.

Analytically the slope of the tangent can be given as $-\xi \bar{S}_{\max}$.

Since $u_{1,\text{opt}}$ has been determined and now it is z_{opt} which is to be determined. For external and internal surfaces the optimal parameters of equations (28) and (29) are given,

$$(\mu_{\text{opt}})_{\text{ext}} = \frac{37}{192} \frac{1.0 - u_{1,\text{opt}}}{\phi_1^2 u_{1,\text{opt}}} = \delta_{\text{ext}} \quad \dots (41)$$

and

$$(\mu_{\text{opt}})_{\text{int}} = \frac{19}{192} \frac{(1.0 - u_{1,\text{opt}})}{\phi_1^2 u_{1,\text{opt}}} = \delta_{\text{int}} \quad \dots (42)$$

Putting the values of the above optimized parameters into equations (28) and (29), we have,

$$\delta_{\text{ext}} = \int_{(z_{\text{opt}})_{\text{ext}}}^{1.0} z^{-2} dz$$

Or,

$$(z_{\text{opt}})_{\text{ext}} = \frac{1}{1.0 + \delta_{\text{ext}}} \quad \dots (43)$$

and

$$\delta_{\text{int}} = \int_{0.5}^{(z_{\text{opt}})_{\text{int}}} z^{-2} dz$$

Or,

$$(z_{\text{opt}})_{\text{int}} = \frac{1}{2.0 - \delta_{\text{int}}} \quad \dots (44)$$

Thus the optimal length of location of a thin layer inside the catalyst is given by equations (43) and (44) for external and internal surfaces respectively. It is also clear

from the above equations that as the thiele modulus increases, the optimal location shifts towards the surface, and at very high values of the thiele modulus, the whole layer shifts at the surface, thus the egg shell type distribution is the best at these conditions.

STEP DISTRIBUTION:

Practically it may not be possible and also from catalyst dispersion and sintering viewpoints, to locate all the active catalyst at one specific location, as was described in the case of Dirac - delta type distribution. We now examine a more realistic case in which the catalyst is present only in a narrow region and centered, ofcourse, about at the optimal distance as was previously determined for amphora. Now the distribution function is defined by the following equations,

$$a(z) = 0 \quad z < z_{opt} \text{ or } z > z_1 \quad \dots (46)$$

$$= \beta \quad z_{opt} < z < z_1 \quad \dots (47)$$

$$\text{where} \quad z_{opt} = \bar{z} - \Delta \quad \dots (48)$$

$$\text{and} \quad z_1 = \bar{z} + \Delta \quad \dots (49)$$

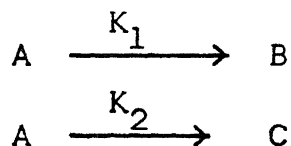
where Δ is the width of the step function.

We define the β such as to satisfying the requirement of equation (12). Thus β comes out to be

$$\beta = \frac{7}{8} \left(\frac{1.0}{z_1^3 - z_{opt}^3} \right) \quad \dots (50)$$

SIMULTANEOUS REACTIONS:

Consider the following case of parallel first order, isothermal reactions with negligible external mass transfer resistance,



With the rate constants K_1 and K_2 . The steady state mass balance equations, in the nondimensional form, with the dimensionless variables as were defined in the case of consecutive reactions are given,

$$\frac{1}{z^2} \frac{d}{dz} \left(z^2 \frac{du_1}{dz} \right) = (\phi_1^2 u_1 + \frac{1}{\xi} \phi_2^2 u_2) a(z) \quad \dots (51)$$

$$\frac{1}{z^2} \frac{d}{dz} \left(z^2 \frac{du_2}{dz} \right) = \phi_1^2 u_1 a(z) \quad \dots (52)$$

And the non dimensional boundary conditions are given by the following relations,

$$u_1(1) = u_1(0.5) = 1.0 \quad \dots (53)$$

$$u_2(1) = u_2(0.5) = u_2^0 \quad \dots (54)$$

The global selectivity \bar{S} is defined by equation (17) and (18). Application of the steady state mass balance equations into equation (17) and (18) gives the relation for the global selectivity for simultaneous reactions as follows:

$$\bar{S} = \frac{\int_{0.5}^{1.0} \xi \phi_1^2 u_1 a(z) z^2 dz}{\int_{0.5}^{1.0} (\xi \phi_1^2 u_1 + \phi_2^2 u_2) a(z) z^2 dz} \quad \dots (55)$$

The steady state mass balance equation with $a(z)$ (as defined by equation (25)) are solved by shooting method (described in chapter 3) and the selectivity for uniform and linear, parabolic distribution has been evolved by using equation (49). The results are given in chapter (4).

The effectiveness factor for simultaneous reactions is given by their defining relationship which reduces to ,

$$\eta = \frac{30}{7} \frac{1}{\phi_1^2} \int_{0.5}^{1.0} (\phi_1^2 u_1 + \frac{1}{\xi} \phi_2^2 u_2) z^2 a(z) dz \quad \dots (56)$$

and the yield,

$$Y = \eta \bar{S} \quad \dots (57)$$

The results are discussed in chapter (4).

DIRAC-DELTA TYPE DISTRIBUTION:

The Dirac-delta type distribution is defined by equation (26) and the optimization technique is also the same as was described in the case of consecutive reactions. But the optimal parameters differ that of the consecutive case. The maximum selectivity is given by the following equation.

$$\bar{S}_{\max} = \frac{u_{1,\text{opt}} \phi_2^2}{u_{1,\text{opt}} \phi_1^2 + \phi_2^2 u_{2,\text{opt}}} \quad \dots (58)$$

Where $u_{1,\text{opt}}$ is the value of u_1 , which maximizes the selectivity function and hence the optimal Dirac distribution is given

$$a(z)_{\text{opt}} = \frac{\delta(z-z_{\text{opt}})}{\frac{24}{7} z^2} \quad \dots (59)$$

and thus the maximum global selectivity can be obtained by a Dirac-delta type distribution and the optimal distance to apply the thin layer of the active sites is given,

$$(z_{\text{opt}})_{\text{ext}} = \frac{1.0}{1 + \delta_{\text{ext}}^*} \quad \dots (60)$$

$$(z_{\text{opt}})_{\text{int}} = \frac{1.0}{2.0 - \delta_{\text{int}}^*} \quad \dots (61)$$

where

$$\delta_{\text{ext}}^* = \int_{(z_{\text{opt}})_{\text{ext}}}^{1.0} z^{-2} dz = \frac{39.0}{192.0} \frac{(1.0 - u_{1,\text{opt}})}{(\phi_1^2 + \phi_2^2/\epsilon) u_{1,\text{opt}}} \quad \dots (62)$$

$$\delta_{\text{int}}^* = \int_{0.5}^{(z_{\text{opt}})_{\text{int}}} z^{-2} dz = \frac{17.0}{192.0} \frac{(1.0 - u_{1,\text{opt}})}{(\phi_1^2 + \phi_2^2/\epsilon) u_{1,\text{opt}}} \quad \dots (63)$$

Again the egg shell type distribution is the best when thiele parameters are very high.

CHAPTER 3

METHOD OF SOLUTION

In formulation of the problem we got two system of differential equations, one for consecutive reaction, equation (6) and (7) along with the boundary conditions (8) and (9) and the other for simultaneous reactions, equations (51) and (52) along with the boundary conditions (53) and (54). These are highly nonlinear equations, and the analytical solutions are not possible. We employed the numerical techniques to solve these problems, which provide fairly accurate results.

Number of approximate methods are available for solution of differential equations. They can be classified under two categories,

- (1) Method of weighted residuals.
- (2) The variational method.

In the method of weighted residuals one works directly with the differential equations and boundary conditions whereas in variational method one uses a functional related to differential equation and boundary conditions, i.e., the solution is expanded in terms of a trial function with undetermined constants or functions. The method of weighted residuals provides a framework to compare and elucidate the features of individual method, which it encompasses e.g. collocation, Galarkin, integral etc.

Variational methods are not applicable to all problems and thus suffer a lack of generality. Sometimes they provide powerful results, such as upper and lower bounds on qualities of interest.e.g.,a complementary variational principle method gives correct bounds to effectiveness factor. Further, methods of weighted residuals are easy to apply whereas variational methods require more mathematical manipulations.

For the above reasons, the method of weighted residuals is considered here, though all the approximate solutions satisfy only part of the conditions of the problem; for example the differential equation may be solved at few positions, rather than at each point. The method of weighted residuals encompasses several methods as given above, i.e., collocation, Galarkin, finite difference, finite element, method of moments, the least squares etc. A brief description of these methods is given below.

In the finite difference computations the difference expressions corresponds to a linear interpolation between grid points, When the solution at the grid points is known the solution at other positions is found by linear interpolation. Other more sophisticated schemes are possible. With spline functions, the region between two grid points is interpolated with second or higher degree polynomials. The derivatives at the grid points can be made continuous. Examples of these types of approximations are given by Hall and Watt (15) for integrating non linear ordinary differential equation as two point boundary value problem. The finite element method differs from finite

difference method and other methods, in that with spline functions a low order polynomial is used in each region from x_i to $x_i + \Delta x$. Least squares method minimizes the mean square residuals of the problem. Galarkin's method is similar to collocation method but is very useful for instability or eigen value problems. Galarkin's method requires the evaluation of integrals which could be difficult depending upon nature of integrand, though quadrature method can be applied to ease this problem.

In the collocation technique, it is only necessary to evaluate the residuals at the collocation points, which could be done very easily even if a highly non linear term appears in the differential equation. This method differs in approach from other methods in that it uses a single higher order polynomial over the whole range of interest $x_1 \leq x \leq x_n$, and this polynomial is arranged to satisfy the boundary conditions. This method can be used to initial value problems using Legendre polynomials as spline functions (13). The collocation technique was first advanced by Lanezos. Harvay and spiess (46), used polynomials which were orthogonal on the boundary. Villadsen and Stewart (47) made the major advancement when they developed orthogonal collocation for boundary value problems.

They choose the trial functions to be sets of orthogonal polynomials which satisfied the boundary conditions and the roots of the polynomials gave the collocation points. The orthogonal polynomials were considered because orthogonality takes care of uniqueness of roots and reality of the roots. The

choice of collocation points thus become fixed than arbitrary and the low order collocation results are more dependable. A major simplification can be done if solution is desired in terms of coefficients of trial function. The whole problem is then reduced to a set of matrix equations which are easily generated and solved on computer. Quadrature formulae are also provided which are especially important if the primary information desired from the solution is some integrated property.

Some other specialized methods are also available for the problem of simultaneous diffusion and reaction in catalyst pores. A brief description of these are worth to mention.

The well known quasilinearization technique requires the partial derivatives of right hand side terms of diffusion equation, i.e., reaction rate terms with respect to each variable. For some cases this terms may be such that evaluation of partial derivatives become very difficult, for example in the case of Langmuir- Hinshelwood type of kinetics. Also quasilinearization technique is not suitable where sharp maximum occurs. In another method which is known as invariant embedding, missing condition, usually the slope, at the known point is calculated. The whole region is divided into elements and from the newly calculated first point, a next point is calculated and again the procedure of finding the first point is repeated.

A second order approximation is used to find out the the next point. Agarwal and Saraf (1) have described this. They used the method in solving simultaneous two point boundary value

problems. It is also shown that computer time doubles for each increase in the number of division by one.

CONSECUTIVE REACTIONS:

The non linear two point boundary value problems, as we obtained in chapter 2 are solved by finite difference method, (8,13,15,48).

The application of finite difference method to boundary value problem is straight forward. Any derivative occurring in the differential equation are replaced by their finite difference approximation. The steady state mass balance equations, as were reported:

$$\frac{1}{z^2} \frac{d}{dz} (z^2 \frac{du_1}{dz}) = \phi_1^2 a(z) u_1 \quad \dots (6)$$

can be reduced to

$$\frac{d^2 u_1}{dz^2} + \frac{2}{z} \frac{du_1}{dz} - \phi_1^2 a(z) u_1 = 0 \quad \dots (64)$$

and similarly the mass balance equations for component B can be reduced to ,

$$\frac{d^2 u_2}{dz^2} + \frac{2}{z} \frac{du_2}{dz} - \phi_2^2 a(z) u_2 + \phi_1^2 a(z) u_1 = 0 \quad \dots (65)$$

It is clear from above equations that they are simultaneous. Hence from the equations (64), u_1 can be calculated at the specified values of 'z' and then at this specified value of z, u_2 can be calculated by putting the value of u_1 , in equation (65). The finite difference approximation gives for

equation(64),

$$\begin{aligned} & [(u_1)_{n+1} - 2(u_1)_n + (u_1)_{n-1}] / h^2 - \frac{2}{hxz_n} [(u_1)_{n+1} - (u_1)_{n-1}] \\ & - \phi_1^2 a(z_n)(u_1)_n = 0 \quad \dots\dots (66) \end{aligned}$$

where the mesh is taken uniform and is defined by the following equation,

$$x_n = a + nh, \quad 0 \leq n \leq N \quad \dots\dots (67)$$

$$\text{and} \quad h = \frac{b-a}{N} \quad \dots\dots (68)$$

where b and a are the two boundary points, which are given by equations (8) and (9). It is obvious that we got a band matrix of algebraic equations, which can be solved by a subroutine BAND and the value of $(u_1)_n$ are calculated by the subroutine DIFF1.

Equation (65) may be written in the form of approximate finite difference equations such as:

$$\begin{aligned} & [(u_2)_{n+1} - 2(u_2)_n + (u_2)_{n-1}] / h^2 - 2[(u_2)_{n+1} - (u_2)_{n-1}] / (hxz_n) \\ & + \phi_2^2 (u_2)_n a(z_n) - \phi_1^2 (u_1)_n a(z_n) = 0 \quad \dots\dots (69) \end{aligned}$$

The above equation can be solved by using the subroutine DIFF2 by calling BAND matrix subroutine.

After calculating the values of the u_1 and u_2 equation (21) can be numerically integrated by putting the values of $(u_1)_n$ and $(u_2)_n$ at the difference points z_n , and thus the global selectivity can be calculated.

For isolated solutions of a nonlinear problem the difference scheme has, for sufficiently small h , a unique solution converging to the exact solution if,

- (1) The linearized difference equations are stable and consistant for the linearized problem,
- (2) The linearized difference operator is lipschitz continuous
- (3) The nonlinear difference equations are consistant with the non linear differential equation.

SOLUTION OF THE ALGABRIC EQUATIONS:

If the differential equation and boundary conditions are linear , so are the equations of the discretization. The equations (66) and (69) gives the triple-diagonal set of equations, and the matrix of these equations display the typical structure obtained from finite difference methods. If a low order approximation is used, the matrix will have a narrow band width, but for good accuracy h must be small and the matrix will have large dimensions. The solution of the Band matrix can be obtained by the subroutine BAND.

SIMULTANEOUS REACTIONS:

The mass balance equations (51 and 52), obtained in the case of simultaneous reaction can be solved by

relaxation, invariant embodiment and shooting method. Here we employed the shooting method to solve these boundary value problems.

SHOOTING METHOD:

In the shooting method we choose values for all the dependent variables at one boundary. These values must be consistent with any other boundary conditions for that boundary, but otherwise are arranged to depend on arbitrary free parameters whose values we initially guess. We then integrate the ordinary differential equations by initial value methods, arriving at the other boundary. And then iterate till the approximate solution is arrived.

The steady state mass balance equations,

$$\frac{1}{z^2} \frac{d}{dz} \left(z^2 \frac{du_1}{dz} \right) = (\phi_1^2 u_1 + \frac{1}{\epsilon} \phi_2^2 u_2) a(z) \quad \dots\dots (70)$$

$$\frac{1}{z^2} \frac{d}{dz} \left(z^2 \frac{du_2}{dz} \right) = - (\phi_1^2 u_1 a(z)) \quad \dots\dots (71)$$

with the boundary conditions

$$u_1(1) = u_1(0.5) = 1.0 \quad \dots\dots (72)$$

$$\text{and} \quad u_2(1) = u_2(0.5) = u_2^0 \quad \dots\dots (73)$$

Can be reduced into four first order boundary value problems, such as,

$$\frac{du_1}{dz} = u_3 \quad \dots\dots (74)$$

$$\frac{du_2}{dz} = u_4 \quad \dots\dots (75)$$

$$\frac{du_3}{dz} + \frac{2}{z} u_3 = (\phi_1^2 u_1 + \frac{1}{\epsilon} \phi_2^2 u_2) a(z) \quad \dots (76)$$

$$\frac{du_4}{dz} + \frac{2}{z} u_4 = - (\phi_1^2 u_1 a(z)) \quad \dots (77)$$

with boundary conditions

$$u_1(1) = u_1(0.5) = 1.0$$

$$u_2(1) = u_2(0.5) = u_2^0$$

In shooting method we choose the initial guesses of the remaining variables u_3 and u_4 and define a vector \vec{V} which contain the boundary conditions at the inner surface. These boundary conditions are feed in the form of a subroutine ODIENT.

We define vector \vec{F} on the outer surface. The values are feeded in the form of a subroutine SCORE. As far as the Newton-Raphson is concerned, we are nearly in business. We want to find a vector value \vec{V} which zeros the vector value of \vec{F} . We do it by computing the solution of two linear equations,

$$[\Theta] \delta \vec{V} = - \vec{F} \quad \dots (78)$$

and then adding the correction back

$$\vec{V}_{\text{new}} = \vec{V}_{\text{old}} + \delta \vec{V} \quad \dots (79)$$

and the jacobian is defined as

$$[\Theta]_{ij} = \frac{\partial \vec{F}_i}{\partial \vec{V}_j} \quad \dots (80)$$

To solve the initial value problems fourth order Range Kutta method is employed . The description of which is given in standard texts (13,48).

CHAPTER 4

RESULTS AND DISCUSSIONS

In this section we will discuss the effect of various physiochemical parameters on selectivity, defined by equations (19) and (55), effectiveness factor, given by equations (22] and (56) and yield defined by equations (24) and (57), in the case of consecutive and simultaneous reactions. The range of different parameters studied are given in table (4) and are defined below,

(1) THIELE MODULUS (ϕ)

It is defined as the ratio of reaction rate to diffusion rate. It represents the resistance to diffusion in the pellet. Higher the value of the thiele modulus, means, the reaction is severely diffusion limited. The results show that at higher value of this parameter the effectiveness factor and the selectivity are poor.

(2) ACTIVITY DISTRIBUTION PARAMETER (α)

This parameter gives the distribution of activity in a catalyst. By changing this parameter, we can get the different type of distribution,

| | |
|--------------|--------------------|
| $\alpha = 0$ | uniform |
| $\alpha = 1$ | linear |
| $\alpha = 2$ | parabolic |
| $\alpha > 2$ | other distribution |

The values of α have been varied in the range of 0 to 8. It is found that higher values of α gives higher value of selectivity

and effectiveness factor.

(3) RATIO OF KINETIC CONSTANTS (λ)

was defined by equation (20). We studied the effect of λ on selectivity, effectiveness factor and yield. It is observed that higher value of λ gives poor selectivity, yield and effectiveness factor.

(4) DIMENSIONLESS SURFACE CONCENTRATION OF COMPONENT B (u_2^0)

It is defined as the ratio of surface concentration of component B to the surface concentration of component A. we studied effectiveness factor, selectivity and yield of the consecutive reactions as a function of u_2^0 . We shown that lesser the concentration of u_2^0 , higher is the selectivity and effectiveness factor and yield.

(5) RATIO OF DIFFUSION COEFFICIENTS (ξ)

It is defined as De_1/De_2 , where De_1 and De_2 are the effective diffusivities of the components A and B respectively. The effect of ξ has been studied in the range of 0.1 to 10.0. It was found that at higher values of this parameter, selectivity and yield can be improved.

Table - 4
RANGE OF PARAMETERS STUDIED

| Parameter | Range |
|--|------------|
| 1. ϕ , Thiele modulus | 0.1-100 |
| 2. α , Activity distribution parameter | 0 - 8 |
| 3. λ , ratio of kinetic constants | 0.1 - 1.0 |
| 4. u_2^0 , dimensionless surface concentration of component B | 0 - 1.0 |
| 5. ξ , ratio of diffusivities | 0.1 - 10.0 |

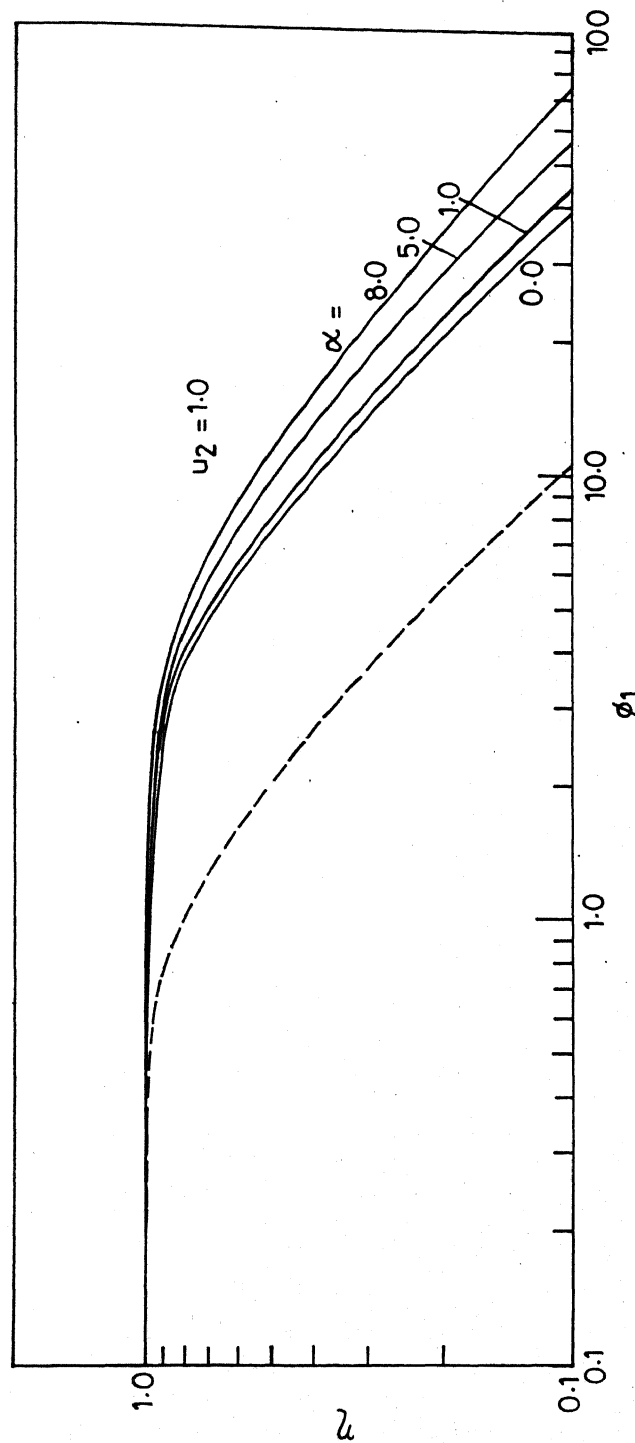


Fig. 4 -Effect of thiele modulus on effectiveness factor on varying activity for series α_1 first order reaction. Discontinuous curve is for uniformly active sphere.

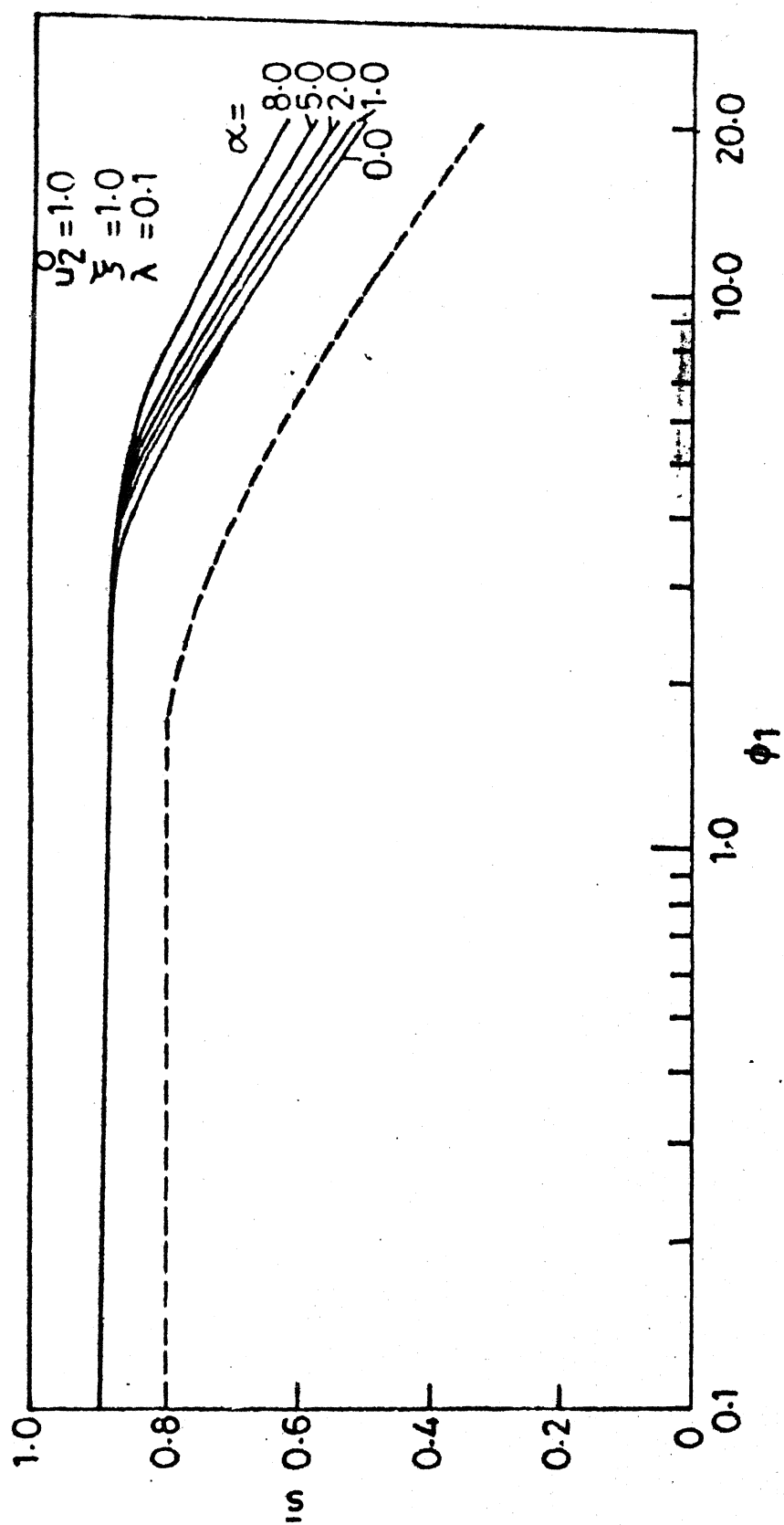


Fig. 5 - Global selectivity vs. thiele modulus for series reaction on amphora catalyst. Discontinuous curve shows the \bar{s} for sphere.

CONSECUTIVE REACTIONS:

The effectiveness factor as a function of thiele parameter is given in figure (4), with α as a second parameter. The uniform activity distribution ($\alpha=0$) gives the lower value of effectiveness factor, as the value of α is increased, the effectiveness factor increases for all values of thiele parameter. When the thiele parameter is less than unity, effectiveness factor is close to unity. At higher value of thiele parameter ($\phi > 3$), the effectiveness factor decreases linearly with thiele parameter. The results on amphora catalyst has been compared with a conventional spherical pellet, and it has been found that we can improve the effectiveness factor tremendously by using amphora shape, at higher value of thiele modulus. At $\phi_1=10$, η exhibited by an sphere is only 0.11, while its value is 0.4 for uniformly active amphora and 0.55 for non uniformly active amphora ($\alpha=8$).

Figure (5) gives the selectivity as a function of thiele modulus for different values of α , Keeping u_2^0 , ξ and λ as constants. It is clear from the figure that as thiele modulus increase i.e., the reaction is severely diffusion limited, the selectivity decreases. But it can be improved by increasing the value of α . It represents that when the diffusion is severe, the activity should be at the decreasing order towards the centre of the pellet.

For the same value of u_2^0 and ξ , but different value of λ (the ratio of kinetic constants K_2 and K_1) the results are

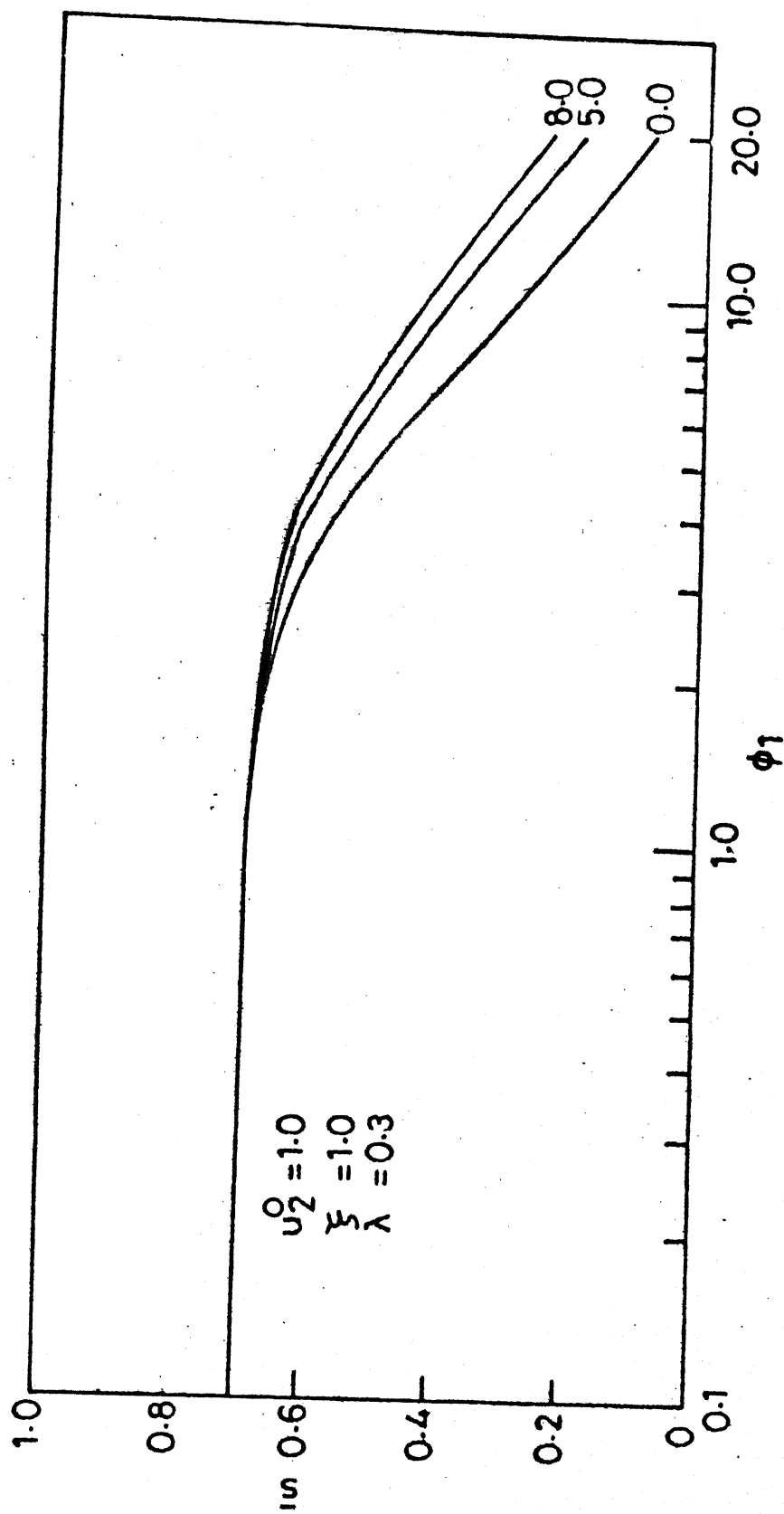


Fig. 6 - Global selectivity vs. Thiele modulus for series reaction on amphora catalyst.

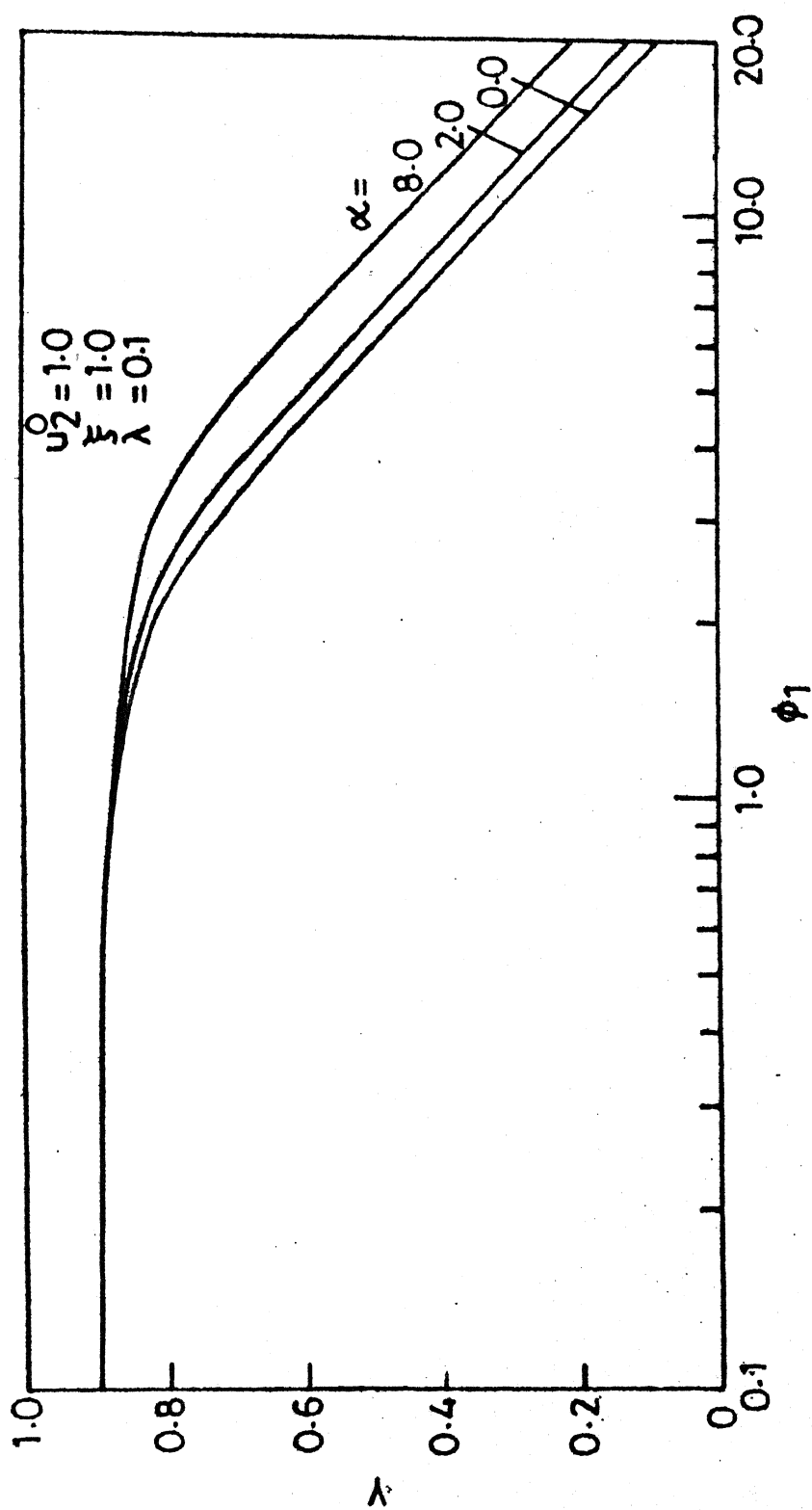


Fig. 7 -Effect of thiele parameter on yield for series reactions.

Plotted in figure (6). The value of selectivity decreases when the value of λ is increased from 0.1 to 0.3. It is also observed that the parameter α becomes more effective at higher value of ϕ .

Fig. (7) shows the yield of component B in consecutive reactions as a function of thiele parameter for different values of α . (The value of $u_2^0 = 1.0$, $\xi = 1.0$, and $\lambda = 0.3$) and Fig. (8) for ($u_2^0 = 1.0$, $\xi = 1.0$ and $\lambda = 0.5$). These two figures show a marked reduction of yield for high value of thiele parameter. Increasing the value of α increases the yield, as before.

In Fig. (9) selectivity is plotted as function of u_2^0 (The dimensionless surface concentration of component B), for different values of α , at $\phi_1 = 10.0$. When the surface concentration is zero, selectivity is high and it continuously decreases, when the surface concentration increases. This effect is important as in actual reactors, as the reaction proceeds, the value of u_2^0 increases, and the selectivity, in the reactor goes down. The effect of change of u_2 on yield is shown in Fig. (10).

Fig. (11) and (12) shows the effect of changing the value of ξ (The ratio of diffusion coefficients) on selectivity and yield respectively. With increase in the value of ξ the value of selectivity and yield increases, also increasing the value of α improves both selectivity and activity.

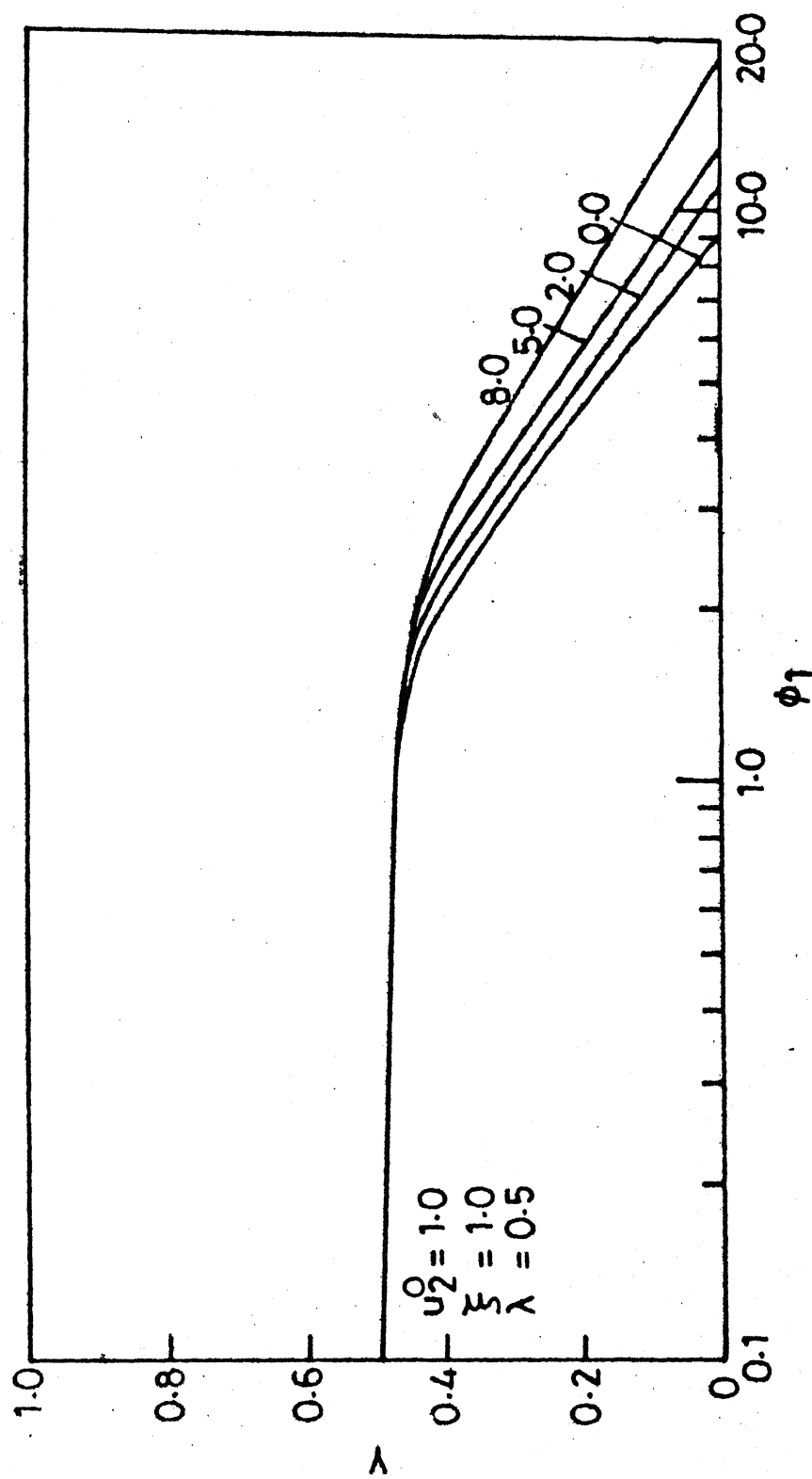


Fig. 8 - Effect of thiele parameter on yield for series reactions.

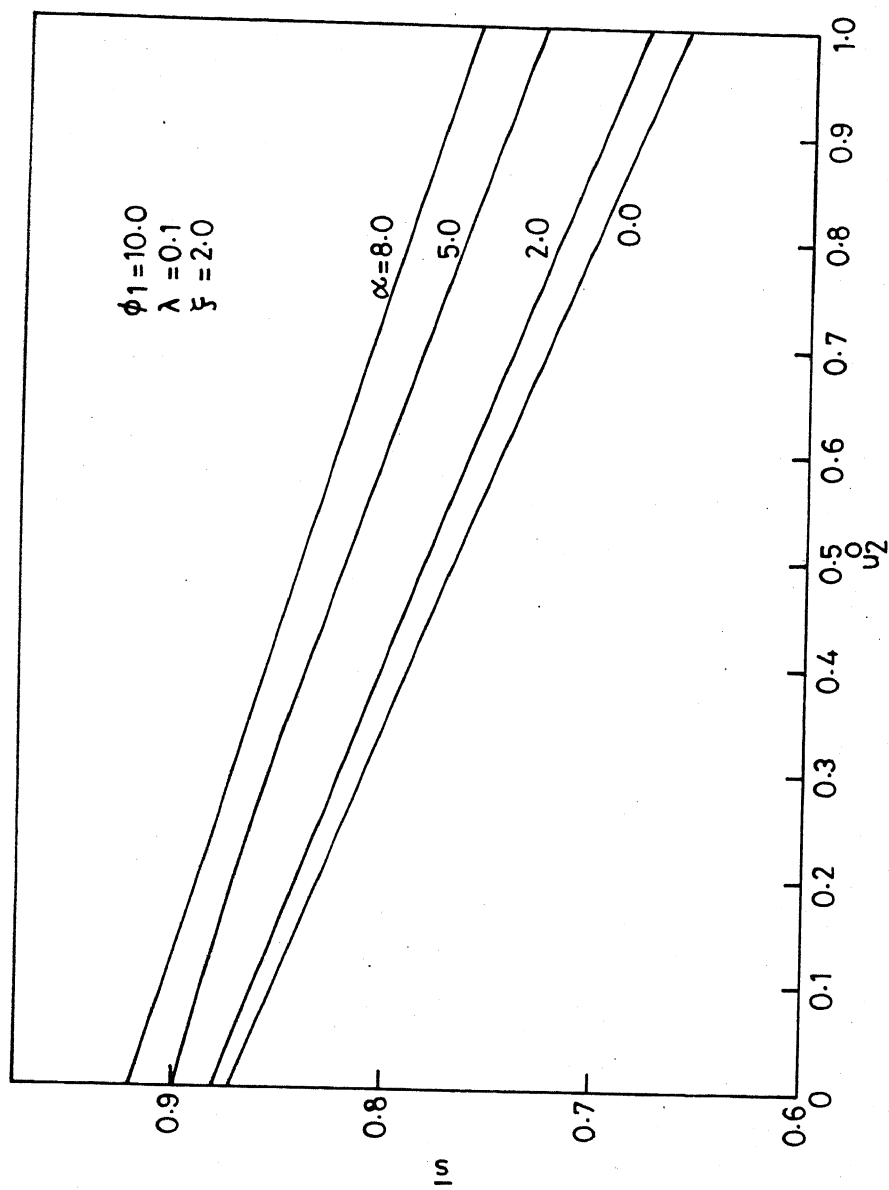


Fig. 9 - Selectivity vs. dimensionless concentration of component B
curve for series reactions.

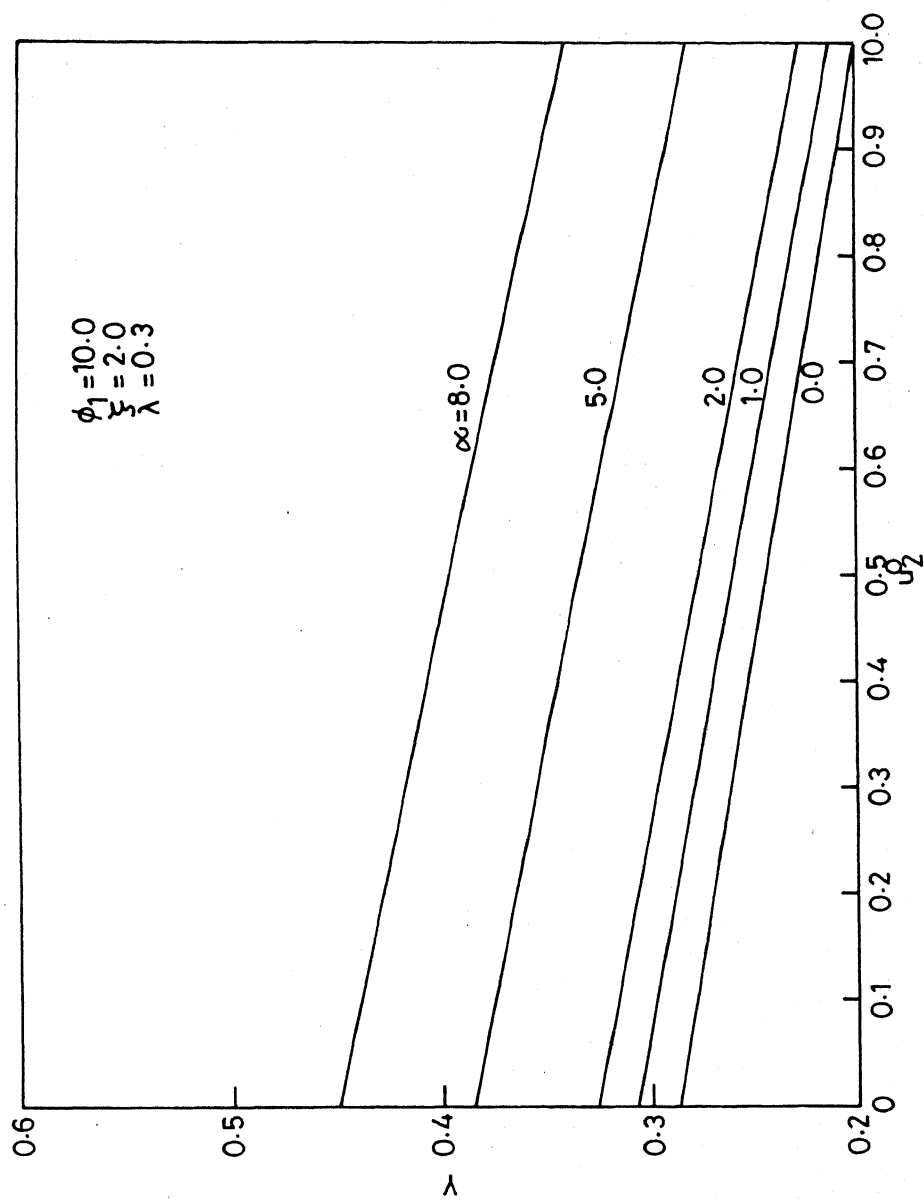


Fig. 10 -Effect of dimensionless concentration of component B on the yield for series reactions.

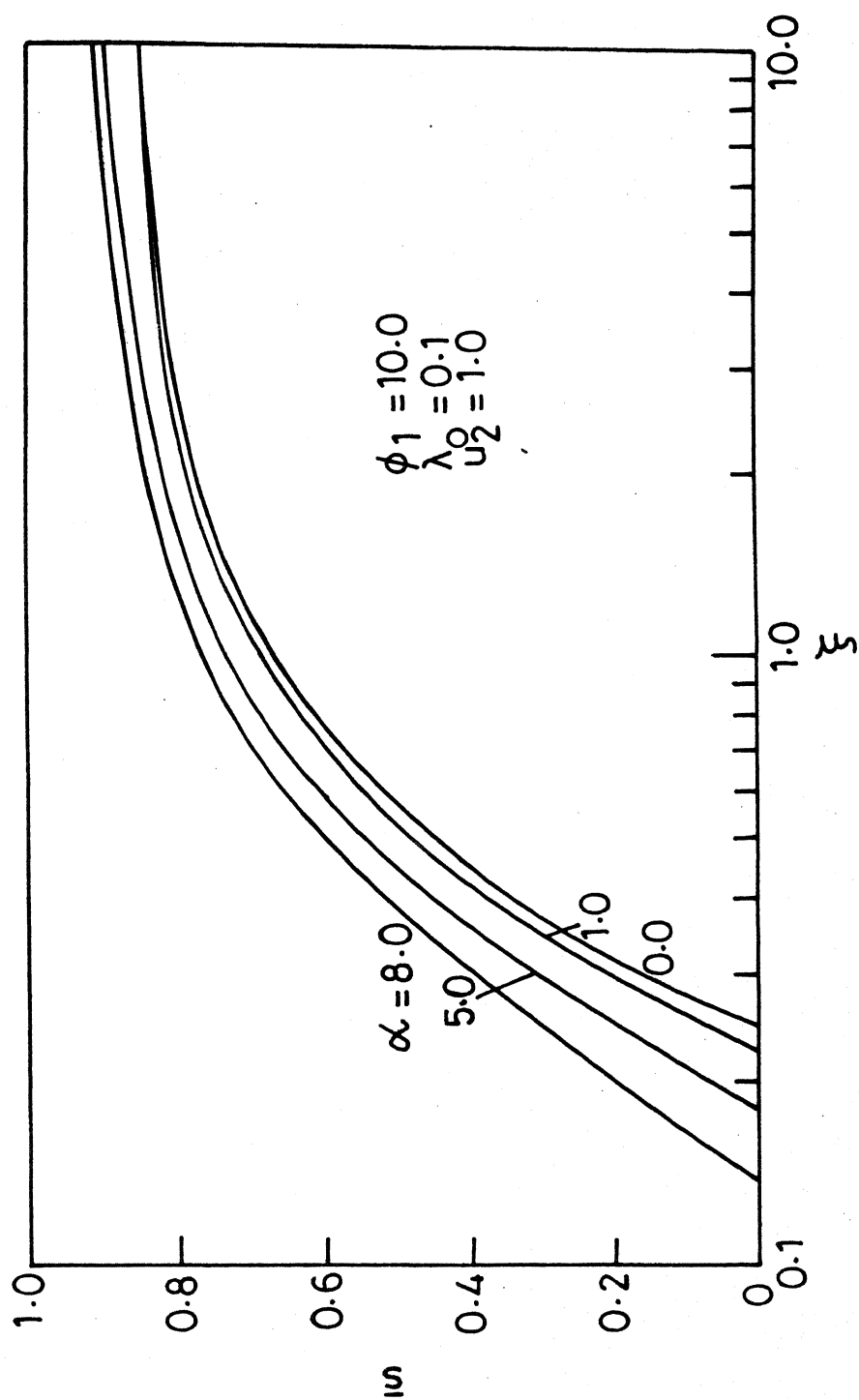


Fig. 11 -Selectivity vs. ratio of diffusivities curve for series reactions.

Fig.(13) gives the effect of varying the value of λ (the ratio of kinetic constants K_1 and K_2) on selectivity for given values $\phi_1=10.0$, $\xi=1.0$ and $u_2^0=0.5$. The results shows that when the value of λ is increased, the selectivity decreases. Also at high values of α , the selectivity is high.

SIMULTANEOUS REACTIONS

The effect of changing thiele parameter ϕ_1 and α (the activity distribution parameter) on effectiveness factor η is shown in Fig. 14 for $u_2^0 = 1.0$, $\xi=1$ and $\lambda = 0.1$. The figure shows that as the thiele parameter is increased the activity decreases and at higher values of thiele parameter ($\phi > 3$) the effectiveness factor decreases proportionally with ϕ . The value of effectiveness factor increases by increasing the value of α .

Fig. 15 gives the selectivity as a function of thiele parameter for two value of α when $u_2 = 0$, $\xi = 1.0$, $\lambda = 0.1$. This figure shows that selectivity is nearly unity at low value of ϕ but decreases by small amount at higher values of ϕ , (Thele parameter), which is obvious also since both the reactions are of first order Fig. 16 gives the yield for the above case.

Fig.(17) gives the selectivity as a function of u_2^0 . At lower values of u_2^0 , the selectivity is high and it continuousl decreases, when the value of u_2^0 increases.

DIRAC-DELTA TYPE DISTRIBUTION

The global selectivity is much higher in Drac-delta, than the global selectivity obtained, with other catalyst

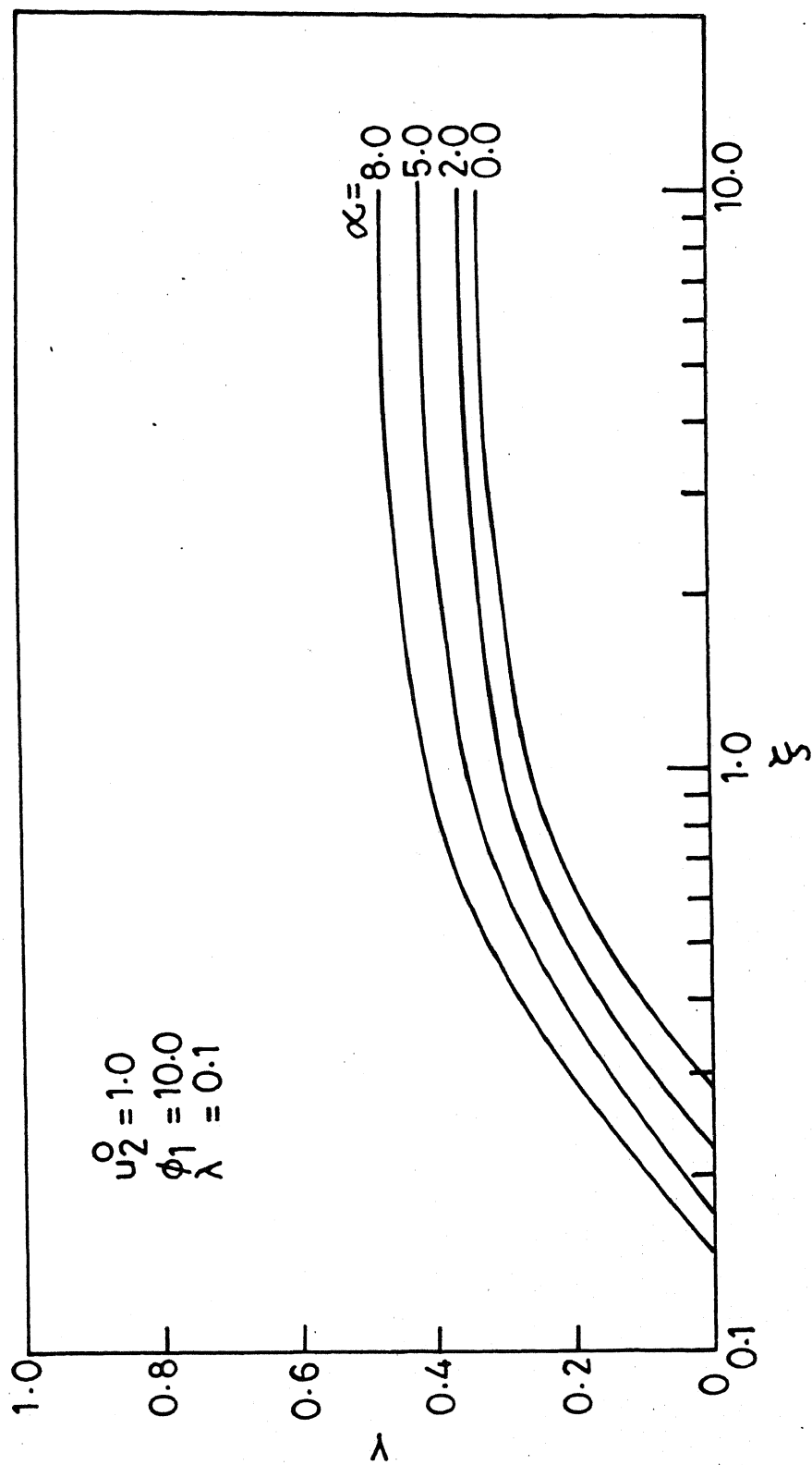


Fig. 12 -Effect of the ratio of diffusivities on yield for series reactions.

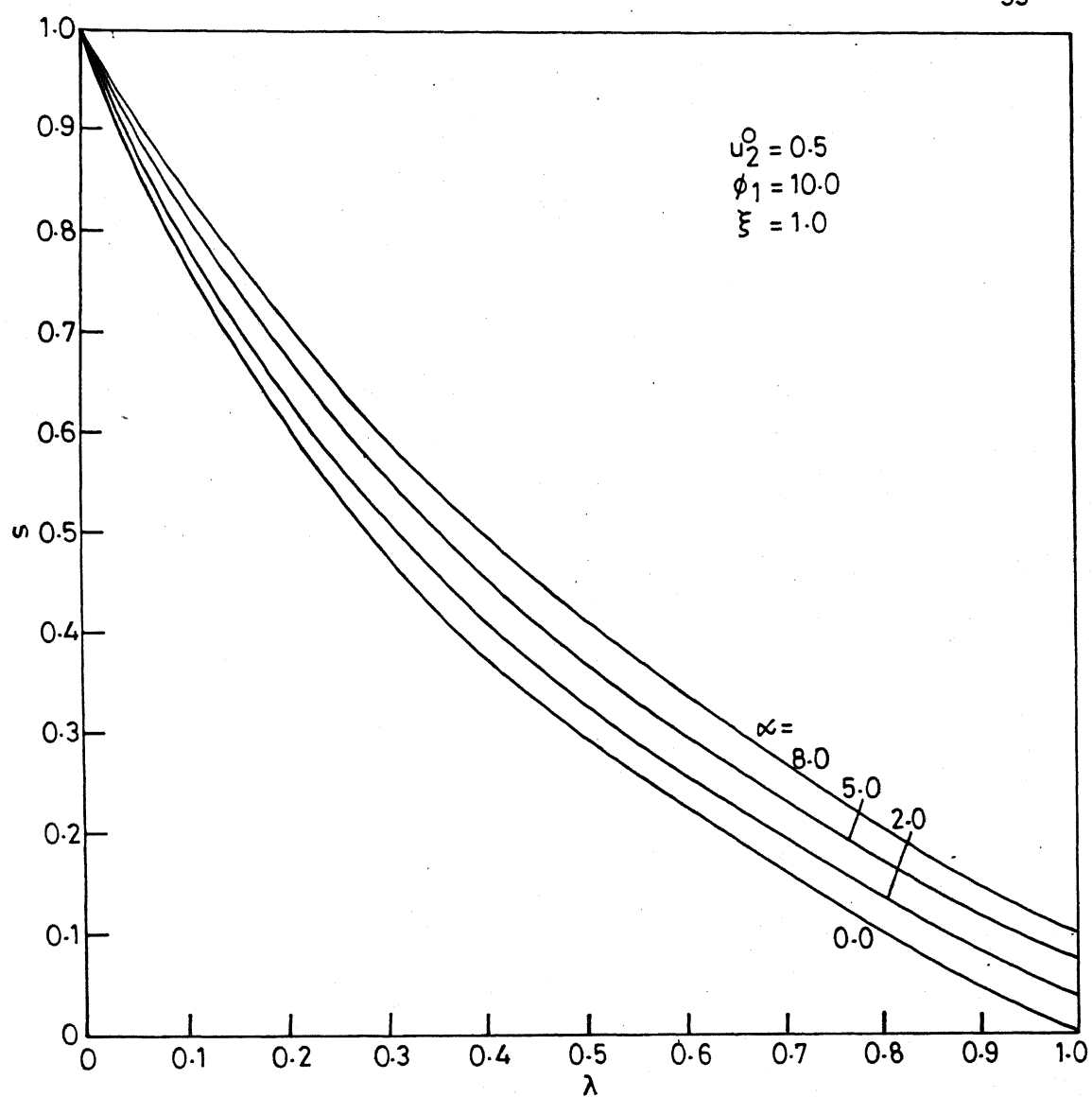


Fig. 13 - Effect of the ratio of thiele parameters on selectivity on varying activity for series reactions.

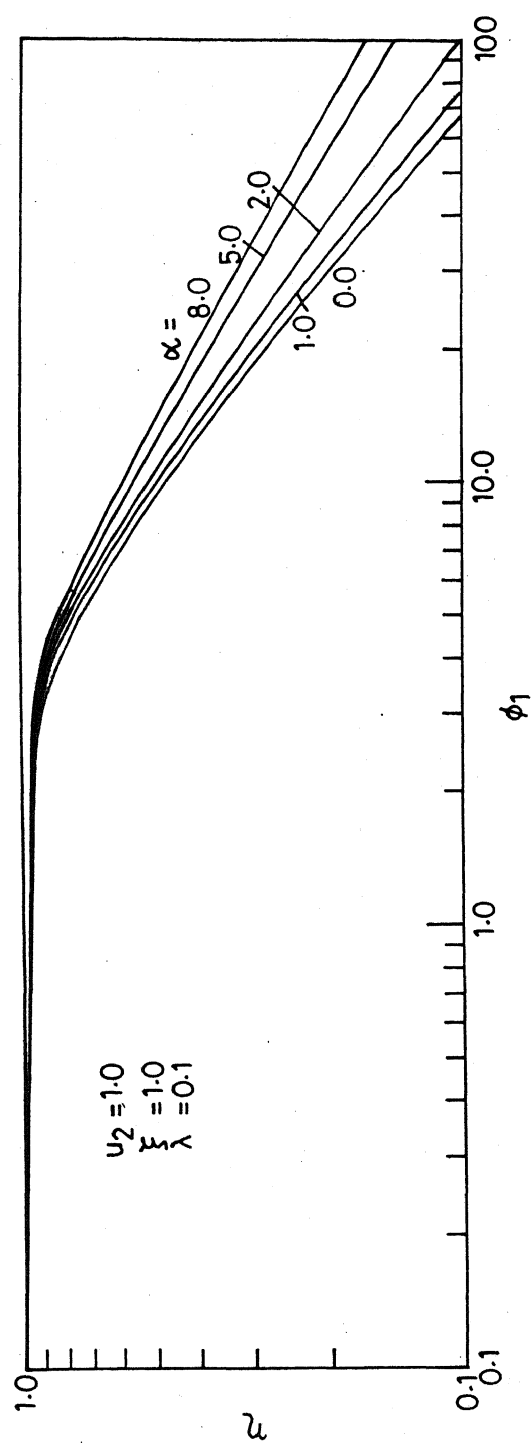


Fig. 14 - Effectiveness factor for first simultaneous reactions with negligible external mass transfer resistance.

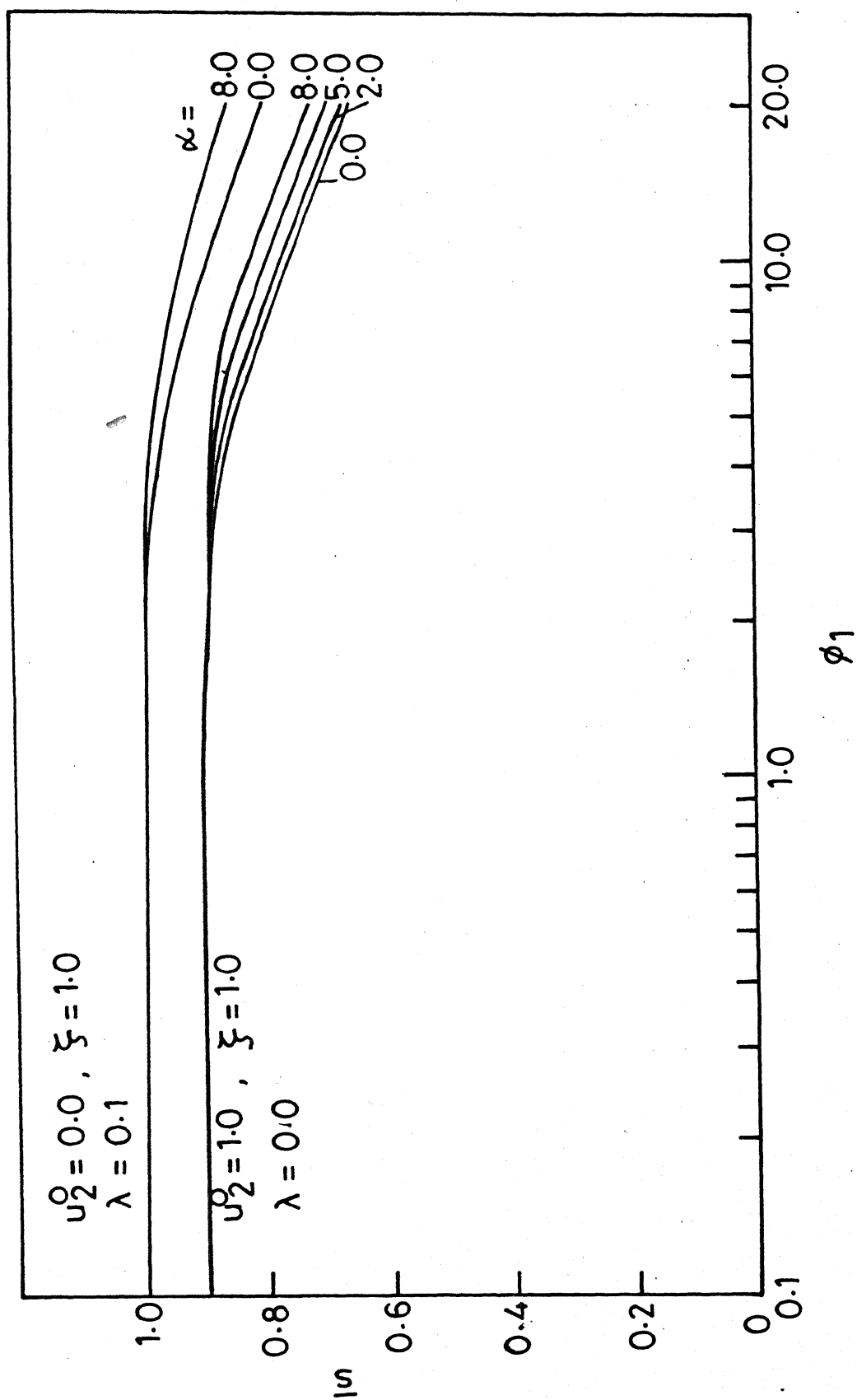


Fig. 15 - Selectivity vs. thiele modulus curve for simultaneous reactions.

distributions such as uniform and linear. This has been shown in Fig (18) that when ($z_{opt}=0.7, \lambda =0.1, u_2^0=1.0, \kappa=1.0$) the selectivity vs thiele modulus curve gives about 98% selectivity. As is shown in Fig.(19) that distance z_c , where the active components are applied, is a function of thiele parameter. If thiele parameter is higher than the specified value, the selectivity becomes zero.

Fig. (19) shows the z_{opt} as a function of thiele parameters at ($\kappa=1.0, \xi=1.0, u_2^0=1.0$). It is shown that when the reaction is kinetic controlled, the whole active sites should be situated at the centre of the pellet, the 'egg yolk' type distribution. As the thiele modulus is high ($\phi > 6.0$) the optimal strategy is to apply the sites over the surface.

EFFECTS OF THE PHYSIOCHEMICAL PARAMETERS IN GENERAL

EFFECT OF u_2^0 :

The effect of u_2^0 on selectivity, effectiveness factor and yield on both the parallel and series reactions is much telling. In case of the series reactions it plays an important role. Initially if u_2^0 is zero, in the case of series reactions, the selectivity is high and it can never be negative. Higher the value of u_2^0 , in any case, lower will be the selectivity, effectiveness factor and yield of the reactions. So it is suggested that initially there should be no surface concentration of the component B. The effect of component B is more telling

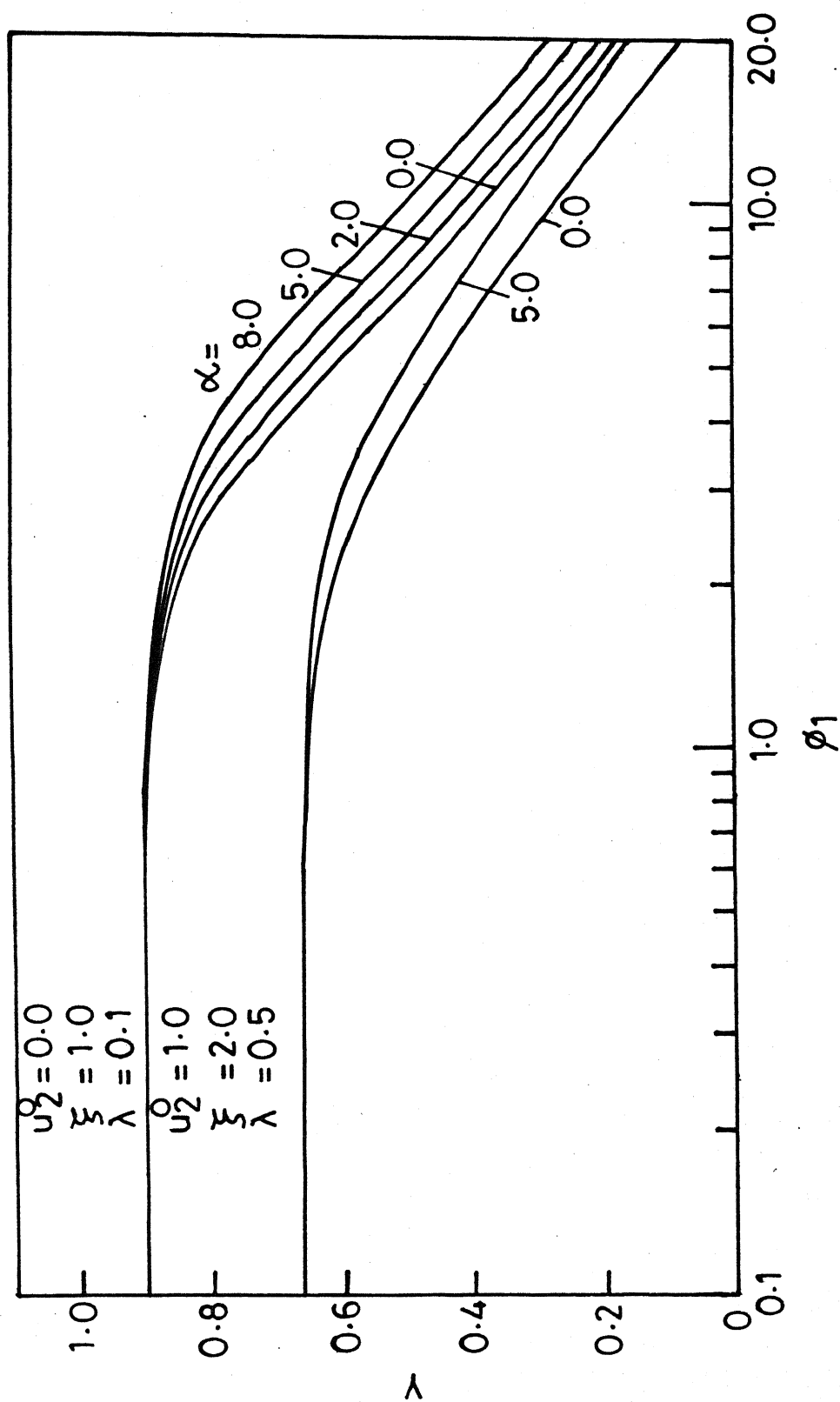


Fig. 16 -Yield of the desired product vs. thiele modulus curve
for simultaneous reactions.

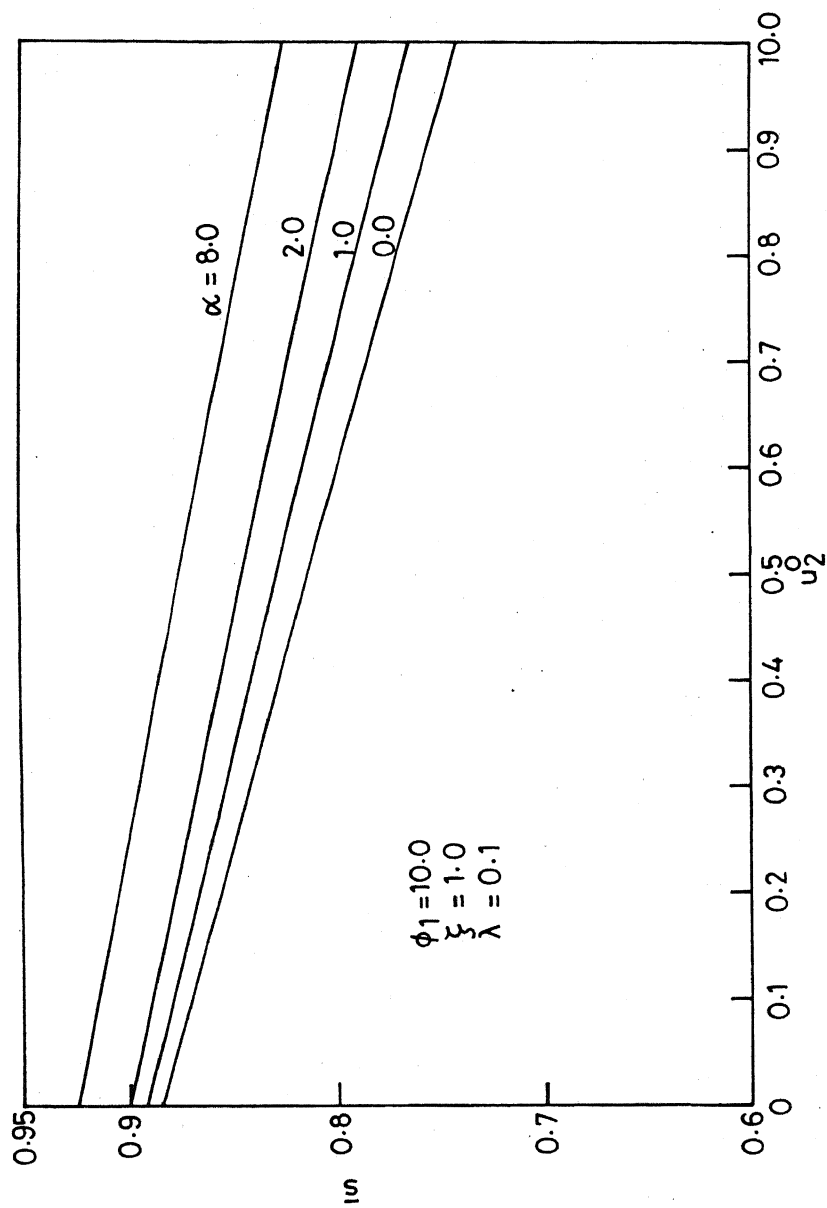


Fig. 17 - Effect of the dimensionless concentration of component B on the yield for simultaneous reactions.

in case of series reactions, since component B further dissociates into the other components.

EFFECT OF λ :

λ is the ratio of the squares of the thiele modulus of the reactions. When λ is constant, it reduces to the ratio of the kinetic parameters K_2 and K_1 . At lower value of this parameter we obtained higher values of selectivity and yield. The effect of λ is more telling in the case of series reactions. When $\lambda = 1$, tends that $K_1 = K_2$ and hence the selectivity becomes zero. At higher values the selectivity becomes negative. But it can be improved, by using the Dirac-delta type distribution.

EFFECT OF ξ :

ξ is a dimensionless parameter defined as the ratio of the effective diffusivity of component A to the effective diffusivity of component B. At lower value of this parameter we got lower selectivity and the effectiveness factor.

EFFECT OF α :

α is a parameter defining the activity distribution. When $\alpha=0$ the distribution is uniform, $\alpha=1$, the distribution is called linear, $\alpha=2$, the distribution is said to be parabolic. The higher value of the α represents that the activity is highly decreasing towards the centre of the pellet. As α

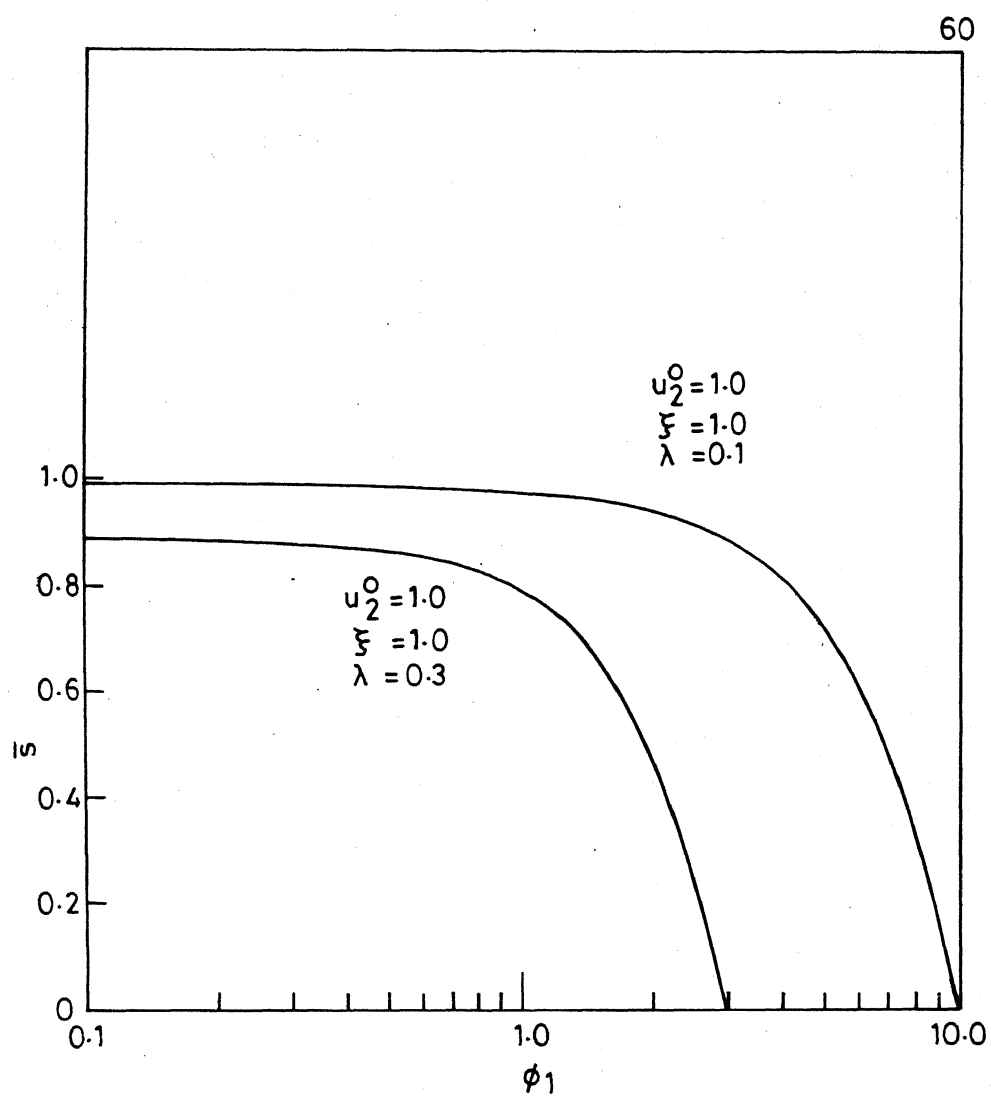


Fig. 18 -Selectivity vs. ϕ curve for series reaction
when the distribution is Dirac-delta type.

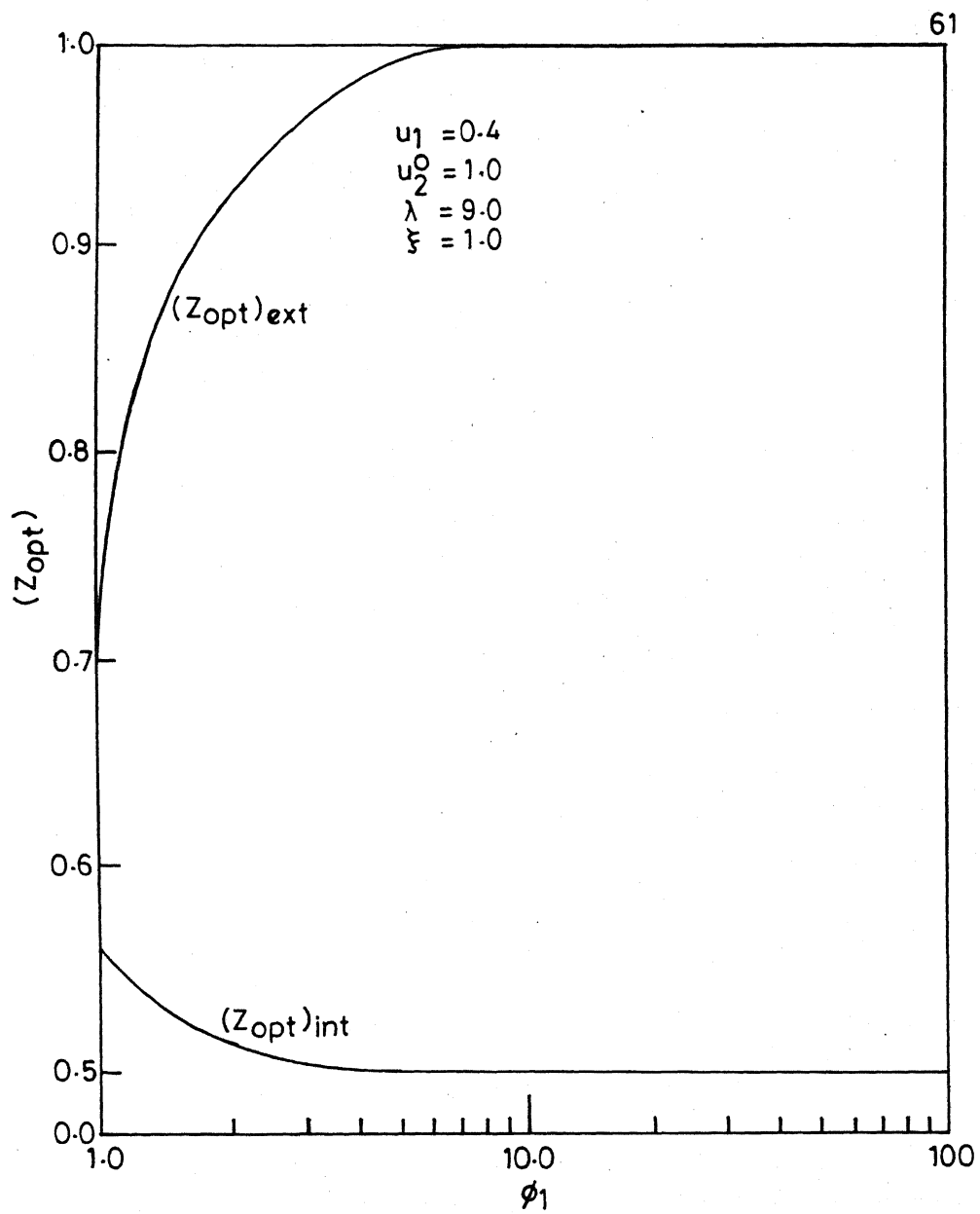


Fig. 19 - Variation of optimal location against the thiele modulus Dirac -delta distribution.

increases, selectivity yield and effectiveness factor is being increased. It effects, highly the parallel reactions, as it is clear from the Figures(4)-(10).

COMPARISION WITH THE SPHERE:

We compared the effectiveness factor and global selectivity obtained on the new shape, with sphere. It was found that at lower value of the thiele modulus, at the same operating conditions, both the sphere and the amphora exhibit the same values of effectiveness factor. But as thiele modulus increases, the amphora shape exhibits tremendously improved values of the thiele modulus. Regarding the selectivity, amphora catalyst, produces always, better results, at any operating condition. The comparision is made in Fig. (4) and (5).

COMPARISION BETWEEN CONSECUTIVE AND SIMULTANEOUS REACTIONS:

The non uniformly active catalyst exhibit improved selectivity in both the cases . But the effectiveness factor, changes much faster with changing the activity distribution parameter in the case of simultaneous reaction than the case of consecutive reactions, but the yield and the selectivity changes tremendously in the case of consecutive reactions. It is due to that the selectivity in case of the consecutive reactions, depends very much of the intermediate product, since this component, decomposes further, to produce the non desired product. While in the case of simultaneous reactions, it is not so.

CHAPTER 5

CONCLUSIONS

Amphora catalyst pellet gives better activity selectivity and yield for consecutive reactions in comparison to spherical catalyst pellet. (e.g. $\phi_1=10.0$, $\eta=0.4$ and $\bar{S} = 0.66$ for amphora and $\eta= 0.11$ and $\bar{S}= 0.49$ for spherical pellet). It gives higher selectivity in comparison to the conventional spherical pellet due to small diffusion path and low residence time of intermediates in the pellet. Thus for consecutive reactions it plays an important role at high values of the thiele parameter.

It has been found that the amphora type pellet gives better activity, selectivity and yield for consecutive reactions. As the value of the activity distribution parameter is increased for 0 to a high value, there is an increase in activity selectivity and yield. (e.g., at $\alpha = 0$, $\eta = 0.4$, $\bar{S} = 0.72$; at $\alpha = 1.0$ $\eta = 0.42$, $\bar{S} = 0.74$)

Among the various types of distributions studied, the Dirac-delta type distribution gives the maximum selectivity, for a specified value of thiele parameter, (at $\xi = 1.0$, $\lambda = 0.3$, $u_2^0 = 1.0$ and $\phi_1 = 3.0$ Dirac - delta, 88% selectivity in comparison to the 61% of uniformly active amphora and 63% in comparison to the linear distribution). It gives higher values of selectivity since it exposes the active material to the optimum of the reactants, and thus the secondary reactions can be minimized. This optimal distance is a function of thiele parameter. As the value of the thiele parameter increases, the optimum distance shifts towards the surface and at very high values, the

the strategy is to apply all the active material at the surface, which is known as 'egg shell' type distribution .

RECOMMENDATION FOR THE FUTURE WORK:

The present work can be extended to more realistic cases like external phase mass transfer resistance, non isothermal diffusion and reaction problem, convex and concave type profiles, application of non uniformly active amphora to the reactors, deactivation and ofcourse for a general order kinetics. .

REFERENCES

1. Agarwal, ABL and Saraf, S.K., J. Mathematical Analysis and Applications 72, 524 (1979).
2. Ardiles, D.R. and Castro A.A., Chem. Engg. Commn. 52, 301 (1987).
3. Aris, R., The mathematical Theory of Diffusion and Reaction in Permiable Catalysis Vol-1, Oxford University Press, 1975.
4. Aris, R., Chemical Engineering Science 6, 262 (1957).
5. Becker, E.R., and Wei, J., Jurnal of Catalysis, 46, 365 (1977).
6. Beker, E.R., and Wei, J., Ibid, 46, 372, (1977).
7. Cervello, J. et.al., Chemial Engineering Science 32, 155 (1977).
8. Corbett, W.E. and Luss, D., Ibid, 29, 1473 (1974).
9. Curkierman, A.L., et.al., Ibid, 38, 1977 (1983).
10. DeLancy, G.B., Ibid, 28, 105 (1973).
11. DO, D.D. and Baily, J.E., Ibid, 37, 545 (1982).
12. Dougherty, R.C. and Verykios, X.E., Catal. Rev.- Sci. Engg., 29, 101 (1987).
13. Finlayson, B.A., Nonlinear Analysis in Chemical Engineering, McGraw Hill Inc., 1980.
14. Gottifredi, J.C., et.al., Chemical Engineering Science 36, 713 (1981).
15. Hall, G. and Watt, J.M., Numerical Methods for Ordinary Differential Equations, Claredon Press Oxford, 1976.
16. Harriott, P., Journal of Catalysis, 14, 43 (1969).
17. Herrington, D.R., CHEMTECH, January 1982, pp. 42-47.
18. Harvath, C., and Engasser, J.M., Ind. Eng. Chem. Fundm., 12, 229 (1973).

19. Juang, H.D. and Weng, H.S., Ibid. 22, 224 (1983).
20. Johnson, D.L., and Verykios, X.E., Journal of Catalysis, 79, 156 (1983).
21. Johnson, D.L., and Verykios, X.E., AIChEJ, 30, 44 (1984).
22. Kasaoka, S. and Sakata, Y., Journal of Chemical Engineering of Japan, 1, 138 (1968).
23. Minhas, S. and Carbery, J.J., Journal of Catalysis, 14, 270 (1969).
24. Morbidelli, M. and Servida, A., Ind. Eng. Chem. Fundm., 21, 278 (1982).
25. Morbidelli, M. and Varma, A., Ibid, 21, 284 (1982).
26. Morbidelli, M. and Varma, A., Chemical Engineering Science, 38, 297 (1983).
27. Morbidelli, M. et. al, Journal of Catalysis, 87, 116 (1984).
28. Morbidelli, M., Servida, A., and Varma A., Ind. Eng. Chem. Fundm. 25, 307 (1986).
29. Morbidelli, M., et. al., Ibid, 25, 313 (1986).
30. Reddy Karri, S.B., and Talukdar, J., Chem. Eng. Commn. 52, 127 (1987).
31. Satterfield, C.N., Mass Transfer in Meterogeneous Catalysis, MIT Press, Massachusetts, 1970.
32. Shadman-Yazdi, F., and Petersen, E.E., Chemical Engg. Science, 27, 227 (1972).
33. Smith, T.G., Ind. Eng. Chem. Process Des. Dev., 15, 388 (1976).
34. Thiele, E.W., Ind. Eng. Chem., 31, 916 (1939).
35. Vayenas, C.G. and Pavlov. S., Chemical Engineering Science, 42, 1655 (1987).

36. Vayenas, C.G. and Pavlov, S. Chemical Engineering Science, 42, 2633 (1987).
37. Vayenas, C.G. and Pavlov, S., Ibid, 43, 2729, (1988).
38. Vayenas, C.G. et. al, Catalyst Deactivation, (1987), pp. 459.
39. Wang J.B. and Varma, A., Chemical Engineering Science, 35, 613 (1980).
40. Wang, J.B. and Varma, A., Ibid, 33, 1549 (1978).
41. Wu, H. et.al., Ind. Eng. Chem. Res., 27, 1169 (1988).
42. Yortsos, Y.C. and Tsotsis, T.T., Chemical Engg. Science, 37, 237 (1982).
43. Yortsos, Y.C. and Tsotsis, T.T., Ibid, 37, 1436 (1982).
44. Carberry, J.J., Chemical and Catalytic Reaction Engineering, McGraw Hill Inc., 1976.
45. Petersen, E.E., Chemical Reaction Analysis, Prentice-Hall Inc. Englewood Cliffs, New Jersey, 1965.
46. Horvay, G. and Spiess, F.N., Quart. Appl Maths., 12, 57 (1954).
47. Villadsen, J.V. and Stewart, W.E., Chemical Engineering Science, 22, 1483 (1967).
48. Mc Cormic, J. and Salvadori, M.G., Numerical Methods in Fortran, Prentice Hall Inc, Englewood Cliffs, New Jersey, 1964.

APPENDIX

COMPUTER PROGRAMMES

```

C*****
C      THIS PROGRAMME CALCULATES THE SELECTIVITY,EFFECTIVENESS*
C      FACTOR AND YIELD FOR ISOTHERMAL,FIRST ORDER SERIES      *
C      REACTIONS (A----->B----->C) WITH NEGLIGIBLE EXTERNAL *
C      PHASE RESISTANCE ON NONUNIFORMLY ACTIVE AMPHORA SHAPE. *
C      THE SECOND ORDER, TWO POINT BOUNDARY VALUE PROBLEM HAS *
C      BEEN SOLVED BY USING THE FINITE DIFFERENCE METHOD.      *
C-----*
C      ALPHA IS A COSTT. ALWAYS GREATER THAN ZERO              *
C      ZI IS THE RATIO OF EFFECTIVE DIFFUSIVITIES(DeA/DeB)      *
C      ALEM IS THE RATIO OF THE SQUARES OF THIELE PARAMETERS   *
C      (PHI2/PHI1)**2                                           *
C      PHI1 AND PHI2 ARE THIELE PARAMETERS OF COMPONENTS 'A'   *
C      AND 'B' RESPECTIVELY.                                    *
C*****
      DIMENSION Y1(100), Y2(100),X(100),A1(100,4),A2(100,4)
      COMMON/SAI/ALPHA
      COMMON/BBC/PHI1
      COMMON/CCC/PHI2
      COMMON/ABC/ZI
      COMMON/GDR/Y1
      COMMON/FRG/Y2
      EXTERNAL FN
      REAL H,ALPHA,STRIPS,ZI,ALEM
      OPEN(UNIT=20,FILE='FOR20.DAT')
      OPEN(UNIT=23,FILE='FOR23.DAT')
      READ(20,*)XA,YA1,XB,YB1.
      READ(20,*) N
      READ(20,*) YA2,YB2
      STRIPS=N+1
      H=(XB-XA)/STRIPS
      ALPHA=0.0
1      ZI=1.0
800      ALEM=0.1
700      WRITE(23,111)
          WRITE(23,101)
          WRITE(23,90) YA1
          WRITE(23,120) ALPHA
          WRITE(23,103) ZI
          WRITE(23,104)ALEM
          WRITE(23,200)
          PHI1=0.1
500      X(1)=XA+H
          PHI2=SQRT(PHI1*PHI1*ALEM)
          CALL DIFF1(Y1,N,A1,X,YA1,YB1,H)
          CALL DIFF2(Y2,N,A2,X,YA2,YB2,H)
          CALL SIMPS(SUM1,H,N,XA,XB,X,FN,YA1,YB1,Y1)
          CALL SIMPS(SUM2,H,N,XA,XB,X,FN,YA2,YB2,Y2)
C*****
C      SGLOB IS THE GLOBAL SELECTIVITY DEFINED BY EQN.18$21      *
C      ETA IS THE EFFECTIVENESS FACTOR DEFINED BY EQN.23        *
C      YLD IS THE YIELD OF COMOPONENT 'B' DEFINED BY EQN.24     *
C*****
      SGLOB=1.0-((ALEM*SUM2)/(ZI*SUM1))
      ETA=(24./7.)*SUM1

```

```

      YLD=SGLOB*ETA
      TYPE *,SGLOB,ETA,YLD
      WRITE(23,106) PHI1,SGLOB,ETA,YLD
      IF(PHI1 .LT. 1.0) GO TO 404
      IF(PHI1 .LT. 2.0) GO TO 402
      GO TO 403
402    PHI1=PHI1+1.0
      GO TO 500
403    PHI1=PHI1+2.0
      IF(PHI1 .LE. 20.0) GO TO 500
      GO TO 405
404    PHI1=PHI1*10.0
      GO TO 500
805    ALEM=ALEM+0.2
      IF(ALEM .LE. 1.0) GO TO 700
      ZI=ZI+1.0
      IF(ZI .LE. 3.0) GO TO 800
      ALPHA=ALPHA+1.
      IF(ALPHA .LE. 2.0) GO TO 1
      ALPHA=ALPHA+2.0
      IF(ALPHA .LE. 10.0) GO TO 1
806    FORMAT(10X,F8.3,5X,F9.6,5X,F9.6,5X,F9.6)
101    FORMAT(/20X,23HTHE SELECTIVITY RESULTS//)
103    FORMAT(5X,'ZI=',F9.6)
104    FORMAT(5X,'ALEM=',F9.6/)
200    FORMAT(5X,60(1H-)/12X,'PHI1',9X,'SGLOB',10X,'ETA',11X,'YLD'/
      1 10X,50(1H-))
120    FORMAT(5X,'ALPHA=',F9.6)
90    FORMAT(5X,41HTHE INITIAL CONCENTRATION OF COMPONENT B=,F5.3)
111    FORMAT(20X,25(1H*))
      STOP
      END

```


C THIS SUBROUTINE CALLS THE SUBROUTINE BAND3 AND SOLVES *
 C THE SECOND ORDER BOUNDARY VALUE PROBLEMS.IT GIVES THE *
 C VALUE OF THE CONCENTRATION OF COMPONENT 'A'. *
 C*****
 C*****

```

      SUBROUTINE DIFF1(Y1,N,A1,X,YA1,YB1,H)
      COMMON/BBC/PHI1
      DIMENSION A1(100,4),Y1(100),X(100)
      DO 20 I=1,N
        A1(I,1)=1.0-H/2.*F1(X(I))
        A1(I,2)=- (2.0-H*H*G1(X(I)))
        A1(I,3)=1.0+H/2.*F1(X(I))
        A1(I,4)=H*H*FR1(X(I))
20    X(I+1)=X(I)+H
        A1(1,4)=A1(1,4)-A1(1,1)*YA1
        A1(1,1)=0.0
        A1(N,4)=A1(N,4)-A1(N,3)*YB1
        A1(N,3)=0.0
        CALL BAND3(N,A1,Y1)
      RETURN
      END

```

```

C*****
C      THIS SUBROUTINE CALLS SUBROUTINE BAND3 AND TAKES THE      *
C      VALES OF THE CONCENTRATION OF COMPONENT A FROM THOSE      *
C      CALCULATED BY SUBROUTINE YAP1 AND THEN SOLVES THE        *
C      BOUNDARY VALUE PROBLEM FOR THE CONCENTRAYION OF THE COM*
C      -PONENT 'B'.
C*****
      SUBROUTINE DIFF2(Y2,N,A2,X,YA2,YB2,H)
      COMMON/BBC/FHI1
      COMMON/CCC/FHI2
      COMMON/GDR/Y1
      DIMENSION A2(100,4),Y2(100),X(100),Y1(100)
      DO 10 I=1,N
      A2(I,1)=1.0-H/2.*F1(X(I))
      A2(I,2)=-(2.0-H*H*G2(X(I)))
      A2(I,3)=1.0+H/2.0*F1(X(I))
      A2(I,4)=H*H*Y1(I)*FR2(X(I))
      X(I+1)=X(I)+H
10      CONTINUE
      A2(1,4)=A2(1,4)-A2(1,1)*YA2
      A2(1,1)=0.0
      A2(N,4)=A2(N,4)-A2(N,3)*YB2
      A2(N,3)=0.0
      CALL BAND3(N,A2,Y2)
      RETURN
      END
C*****
C*****
      SUBROUTINE BAND3(N,A,X)
      DIMENSION A(100,4)
      DIMENSION X(100)
      M=N-1
      DO 10 I=2,M
      A(I,2)=A(I,2)*A(I-1,2)-A(I,1)*A(I-1,3)
      A(I,3)=A(I,3)*A(I-1,2)
10      A(I,4)=A(I,4)*A(I-1,2)-A(I,1)*A(I-1,4)
      X(N)=(A(N,4)*A(N-1,2)-A(N,1)*A(N-1,4))/(A(N,2)*
1      A(N-1,2)-A(N,1)*A(N-1,3))
      DO 20 I=1,M
      J=N-I
20      X(J)=(A(J,4)-A(J,3)*X(J+1))/A(J,2)
      RETURN
      END
*****
C      THESE ARE THE GENERALISED FUNCTIONS WHICH ARE BEING      *
C      USED IN THE SUBROUTINES YAP1 AND YAP2.
C*****
C*****
      FUNCTION F1(X)
      F1=2.0/X
      RETURN
      END
C*****
C*****

```

```

        FUNCTION G1(X)
        COMMON/BBC/PHI1
        COMMON/SAI/ALPHA
        PARA1=2.0*(3.0-ALPHA)
        PARA2=(4.0/3.0)*(3.0-ALPHA)
        PARA3=(4.0/3.0)*(3.0+ALPHA)
        IF(X .LE. 0.725) GO TO 20
        GO TO 30
20      G1=-PHI1*PHI1*(19.0/192.)*(3.0-ALPHA)*PARA1*PARA2*
1      (X*(-ALPHA))/(PARA1-PARA2)
        GO TO 40
30      G1=-PHI1*PHI1*(37.0/192.)*(3.0+ALPHA)*PARA3*(X*ALPHA)
1      /(PARA3-1.0)
40      RETURN
        END
C*****
C*****
        FUNCTION G2(X)
        COMMON/CCC/PHI2
        COMMON/SAI/ALPHA
        PARA1=2.0*(3.0-ALPHA)
        PARA2=(4.0/3.0)*(3.0-ALPHA)
        PARA3=(4.0/3.0)*(3.0+ALPHA)
        IF(X .LE. 0.725) GO TO 20
        GO TO 30
20      G2=-PHI2*PHI2*(19.0/192.)*(3.0-ALPHA)*PARA1*PARA2*
1      (X*(-ALPHA))/(PARA1-PARA2)
        GO TO 40
30      G2=-PHI2*PHI2*(37.0/192.0)*(3.0+ALPHA)*PARA3*(X*
1      ALPHA)/(PARA3-1.0)
40      RETURN
        END
C*****
C*****
        FUNCTION FR1(X)
        FR1=0.0
        RETURN
        END
C*****
C*****
        FUNCTION FR2(X)
        COMMON/SAI/ALPHA
        COMMON/BBC/PHI1
        COMMON/ABC/ZI
        PARA1=2.0*(3.0-ALPHA)
        PARA2=(4.0/3.0)*(3.0-ALPHA)
        PARA3=(4.0/3.0)*(3.0+ALPHA)
        IF(X .LE. 0.725) GO TO 20
        GO TO 30
20      FR2=-PHI1*PHI1*ZI*(19.0/192.0)*(3.0-ALPHA)*PARA1
1      *PARA2*(X*(-ALPHA))/(PARA1-PARA2)
        GO TO 40
30      FR2=-PHI1*PHI1*ZI*(37.0/192.0)*(3.0+ALPHA)*PARA3*
1      (X*ALPHA)/(PARA3-1.0)
40      RETURN

```

```

      END
C*****
C      THIS SUBROUTINE INTEGRATES THE EQUATIONS      *
C      BY USING THE SIMPSONS' COMPOSITE RULE.      *
C*****
      SUBROUTINE SIMPS(SUM,H,N,XA,XB,X,FN,YA,YB,Y)
      DIMENSION X(100),Y(100)
      R1=FN(XA)*YA
      R2=FN(XB)*YB
      H0V2=H/2.0
      HALF=FN(XA+H0V2)
      S=0.0
      DO 10 I=1,N
      S=S+Y(I)*FN(X(I))
      HALF=HALF+Y(I)*FN(X(I)+H0V2)
      X(I+1)=X(I)+H
10    CONTINUE
      SUM=(H/6.0)*(R1+R2+4.0*HALF+2.0*S)
      RETURN
      END
C*****
C      ACTIVITY DISTRIBUTION FUNCTION A(X)      *
C*****
      FUNCTION A(X)
      COMMON/SAI/ALPHA
      PARA1=2.0*(3.0-ALPHA)
      PARA2=(4.0/3.0)*(3.0-ALPHA)
      PARA3=(4.0/3.0)*(3.0+ALPHA)
      IF(X .LE. 0.725) GO TO 20
      GO TO 30
20    A=(19.0/192.)*(3.0-ALPHA)*PARA1*PARA2*(X**(-ALPHA))
      1 / (PARA1-PARA2)
      GO TO 40
30    A=(37.0/192.)*(3.0+ALPHA)*PARA3*(X**ALPHA)/(PARA3-1.0)
40    RETURN
      END
C*****
      FUNCTION FN(X)
      FN=A(X)*X*X
      RETURN
      END
*****

```

ENDF600 C*****

```

CALCULATES THE SELECTIVITY,EFFECTIVENESS FACTOR      *
C AND YIELD FOR ISOTHERMAL,FIRST ORDER REACTIONS  A----->B;      *
C A----->C, WITH NEGLIGIBLE EXTERNAL PHASE MASS TRANSFER      *
C RESISTENCE. V(1) AND V(2) ARE THE MISSING BOUNDARY CONDITIONS      *
C AND ALSO THE CONCENTRATION GRADIENTS ON THE SURFACE.THE REMAINING *
C NOMENCLATURE IS THE SAME AS WE UTILISED IN THE LAST PROGRAMME.    *
C*****
      DIMENSION V(2),DV(2)
      COMMON/SAI/ALPHA
      COMMON/BBC/PHI1,PHI2,ZI
      OPEN(UNIT=23,FILE='YY2.OUT')
      YA2=1.0
      ALPHA=0.0
      ZI=1.0
      ALEM=0.1
      WRITE(23,111)
      WRITE(23,101)
      WRITE(23,90)YA2
      WRITE(23,120) ALPHA
      WRITE(23,103) ZI
      WRITE(23,200)
      PHI1=0.1
505    PHI2=SQRT(PHI1*PHI1*ALEM)
      CALL SIMUL(V,DV,EPS,X1,X2,H1,HMIN,N)
      SGLOB=-V(2)/(V(1)*ZI)
      ETA=(24.0/7.0)*V(1)/(PHI1*PHI1+PHI2*PHI2)
      YLD=SGLOB*ETA
      WRITE(*,*)PHI1,SGLOB,ETA
      WRITE(23,106) PHI1,SGLOB,ETA,YLD
      IF(PHI1.LT.1.0) GO TO 404
      IF(PHI1.LT.2.0) GO TO 402
      GO TO 403
402    PHI1=PHI1+1.0
      GO TO 505
403    PHI1=PHI1+2.0
      IF(PHI1.LE.20.0) GO TO 505
      GO TO 405
404    PHI1=PHI1*10.0
      GO TO 505
405    STOP
106    FORMAT(10X,F8.3,5X,F9.6,5X,F9.6,5X,F9.6)
101    FORMAT(/20X,39HTHE SELECTIVITY ON AMPHORA:PARALLEL RXN//)
103    FORMAT(5X,'ZI=',F9.6)
104    FORMAT(5X,'ALEM=',F9.6)
200    FORMAT(5X,60(1H-)/12X,'PHI1',9X,'SGLOB',10X,'ETA',11X,'YLD'/
      1 10X,50(1H-))
120    FORMAT(5X,'ALPHA=',F9.6)
90    FORMAT(5X,41HTHE INITIAL CONCENTRATION OF COMPONENT B=,F5.3)
111    FORMAT(20X,25(1H*))
      END
C*****
C THIS SUBROUTINE CALCULATES THE MISSING BOUNDARY CONDITIONS      *
C V(1) AND V(2) AND RETURNS THEM TO THE MAIN PROGRAMME.          *
C      N2=NUMBER OF MISSING BOUNDARY CONDITIONS                    *

```



```

C      DELTA IS THE PERMISSIBLE ERROR IN THE CALCULATED VALUES      *
C*****
      SUBROUTINE SIMUL(V,DV,EPS,X1,X2,H1,HMIN,N)
      PARAMETER(NVAR=4,N2=2,DELTA=1.0E-3,EPS=1.0E-6,DX=1.0E-4)
      DIMENSION V(2),DELV(2),F(2),DV(2),Y(4)
      OPEN(UNIT=23,FILE='FOR23.DAT')
      V(1)=0.4
      V(2)=0.4
      DELV(1)=DELTA*V(1)
      DELV(2)=DELV(1)
      X1=0.5
      X2=1.0
      H1=0.025
      HMIN=0.0
      N=4
2      CALL SHOOT(NVAR,V,DELV,N2,X1,X2,EPS,H1,HMIN,F,DV)
      IF((ABS(DV(1)).GT.ABS(EPS*V(1))).OR.
*          ((DV(2)).GT.ABS(EPS*V(2)))) GOTO 2
      RETURN
      END
C*****
C      THIS SUBROUTINE CONTAINS THE KNOWN BC'S AT THE INNER SURFACE
C*****
      SUBROUTINE LOAD(X1,V,Y)
      DIMENSION V(2),Y(4)
      Y(1)=1.0
      Y(2)=1.0
      Y(3)=V(1)
      Y(4)=V(2)
      RETURN
      END
C*****
C      THIS SUBROUTINE CONTAINS THE BC'S AT THE OUTER SURFACE
C*****
      SUBROUTINE SCORE(X2,Y,F)
      DIMENSION Y(4),F(2)
      F(1)=Y(3)
      F(2)=Y(4)
      RETURN
      END

      SUBROUTINE DERIVS(X,Y,DYDX)
      COMMON/BBC/PHI1,PHI2,ZI
      DIMENSION Y(4),DYDX(4)
      DYDX(1)=Y(3)
      DYDX(2)=Y(4)
      DYDX(3)=(PHI2*PHI2*Y(2)/ZI+PHI1*PHI1*Y(1))*ACTY(X)-2.0*Y(3)/X
      DYDX(4)=-2.0*Y(4)/X-Y(1)*ZI*PHI2*PHI2*ACTY(X)
      RETURN
      END
C*****
C*****
      SUBROUTINE SHOOT(NVAR,V,DELV,N2,X1,X2,EPS,H1,HMIN,F,DV)
      PARAMETER (NP=20)
      DIMENSION V(N2),DELV(N2),F(N2),DV(N2),Y(NP),DFDV(NP,NP),INDX(NP)

```

```

EXTERNAL DERIVS,RKQC
CALL LOAD(X1,V,Y)
CALL ODEINT(Y,NVAR,X1,X2,EPS,H1,HMIN,NOK,NBAD,DERIVS,RKQC)
CALL SCORE(X2,Y,F)
DO 12 IV=1,N2
  SAV=V(IV)
  V(IV)=V(IV)+DELV(IV)
  CALL LOAD(X1,V,Y)
  CALL ODEINT(Y,NVAR,X1,X2,EPS,H1,HMIN,NOK,NBAD,DERIVS,RKQC)
  CALL SCORE(X2,Y,DV)
  DO 11 I=1,N2
    DFDV(I,IV)=(DV(I)-F(I))/DELV(IV)
11  CONTINUE
  V(IV)=SAV
12  CONTINUE
DO 13 IV=1,N2
  DV(IV)=-F(IV)
13  CONTINUE
CALL LUDCMP(DFDV,N2,NP,INDX,DET)
CALL LUBKSB(DFDV,N2,NP,INDX,DV)
DO 14 IV=1,N2
  V(IV)=V(IV)+DV(IV)
14  CONTINUE
RETURN
END
C*****
C*****
SUBROUTINE RK4(Y,DYDX,N,X,H,YOUT,DERIVS)
PARAMETER (NMAX=10)
DIMENSION Y(N),DYDX(N),YOUT(N),YT(NMAX),DYT(NMAX),DYM(NMAX)
HH=H*0.5
H6=H/6.
XH=X+HH
DO 11 I=1,N
  YT(I)=Y(I)+HH*DYDX(I)
11  CONTINUE
CALL DERIVS(XH,YT,DYT)
DO 12 I=1,N
  YT(I)=Y(I)+HH*DYT(I)
12  CONTINUE
CALL DERIVS(XH,YT,DYM)
DO 13 I=1,N
  YT(I)=Y(I)+H*DYM(I)
  DYM(I)=DYT(I)+DYM(I)
13  CONTINUE
CALL DERIVS(X+H,YT,DYT)
DO 14 I=1,N
  YOUT(I)=Y(I)+H6*(DYDX(I)+DYT(I)+2.*DYM(I))
14  CONTINUE
RETURN
END
C*****
C*****
SUBROUTINE LUDCMP(A,N,NP,INDX,D)
PARAMETER (NMAX=100,TINY=1.0E-20)

```

```

DIMENSION A(NF,NF),INDX(N),VV(NMAX)
D=1.
DO 12 I=1,N
  AAMAX=0.
  DO 11 J=1,N
    IF (ABS(A(I,J)).GT.AAMAX) AAMAX=ABS(A(I,J))
11  CONTINUE
    IF (AAMAX.EQ.0.) PAUSE 'Singular matrix.'
    VV(I)=1./AAMAX
12  CONTINUE
  DO 19 J=1,N
    IF (J.GT.1) THEN
      DO 14 I=1,J-1
        SUM=A(I,J)
        IF (I.GT.1) THEN
          DO 13 K=1,I-1
            SUM=SUM-A(I,K)*A(K,J)
13          CONTINUE
            A(I,J)=SUM
          ENDIF
14        CONTINUE
      ENDIF
      AAMAX=0.
      DO 16 I=J,N
        SUM=A(I,J)
        IF (J.GT.1) THEN
          DO 15 K=1,J-1
            SUM=SUM-A(I,K)*A(K,J)
15          CONTINUE
            A(I,J)=SUM
          ENDIF
          DUM=VV(I)*ABS(SUM)
          IF (DUM.GE.AAMAX) THEN
            IMAX=I
            AAMAX=DUM
          ENDIF
16        CONTINUE
        IF (J.NE.IMAX) THEN
          DO 17 K=1,N
            DUM=A(IMAX,K)
            A(IMAX,K)=A(J,K)
            A(J,K)=DUM
17          CONTINUE
          D=-D
          VV(IMAX)=VV(J)
        ENDIF
        INDX(J)=IMAX
        IF (J.NE.N) THEN
          IF (A(J,J).EQ.0.) A(J,J)=TINY
          DUM=1./A(J,J)
          DO 18 I=J+1,N
            A(I,J)=A(I,J)*DUM
18          CONTINUE
        ENDIF
19      CONTINUE

```

```

        IF (A(N,N).EQ.0.) A(N,N)=TINY
        RETURN
    END
C*****
C   LOWER DECOMPOSITION OF THE MATRICES
C*****
    SUBROUTINE LUBKSB(A,N,NP,INDX,B)
    DIMENSION A(NP,NP),INDX(N),B(N)
    II=0
    DO 12 I=1,N
        LL=INDX(I)
        SUM=B(LL)
        B(LL)=B(I)
        IF (II.NE.0) THEN
            DO 11 J=II,I-1
                SUM=SUM-A(I,J)*B(J)
11          CONTINUE
            ELSE IF (SUM.NE.0.) THEN
                II=I
            ENDIF
        B(I)=SUM
12    CONTINUE
    DO 14 I=N,1,-1
        SUM=B(I)
        IF (I.LT.N) THEN
            DO 13 J=I+1,N
                SUM=SUM-A(I,J)*B(J)
13          CONTINUE
            ENDIF
        B(I)=SUM/A(I,I)
14    CONTINUE
    RETURN
    END
C*****
C*****
    SUBROUTINE ODEINT(YSTART,NVAR,X1,X2,EPS,H1,HMIN,NOK,NBAD,DERIVS,RK
    *QC)
    PARAMETER (MAXSTP=10000,NMAX=10,TWO=2.0,ZERO=0.0,TINY=1.E-30)
    COMMON /PATH/ KMAX,KOUNT,DXSAV,XP(200),YP(10,200)
    DIMENSION YSTART(NVAR),YSCAL(NMAX),Y(NMAX),DYDX(NMAX)
    KMAX=20
    DXSAV=1.0E-3
    X=X1
    H=SIGN(H1,X2-X1)
    NOK=0
    NBAD=0
    KOUNT=0
    DO 11 I=1,NVAR
        Y(I)=YSTART(I)
11    CONTINUE
    XSAV=X-DXSAV*TWO
    DO 16 NSTP=1,MAXSTP
        CALL DERIVS(X,Y,DYDX)
        DO 12 I=1,NVAR
            YSCAL(I)=ABS(Y(I))+ABS(H*DYDX(I))+TINY

```

```

12      CONTINUE
      IF(KMAX.GT.0)THEN
        IF(ABS(X-XSAV).GT.ABS(DXSAV)) THEN
          IF(KOUNT.LT.KMAX-1)THEN
            KOUNT=KOUNT+1
            XP(KOUNT)=X
            DO 13 I=1,NVAR
              YP(I,KOUNT)=Y(I)
13          CONTINUE
            XSAV=X
          ENDIF
        ENDIF
      ENDIF
      IF((X+H-X2)*(X+H-X1).GT.ZERO) H=X2-X
      CALL RKQC(Y,DYDX,NVAR,X,H,EPS,YSCAL,HDID,HNEXT,DERIVS)
      IF(HDID.EQ.H)THEN
        NOK=NOK+1
      ELSE
        NBAD=NBAD+1
      ENDIF
      IF((X-X2)*(X2-X1).GE.ZERO)THEN
        DO 14 I=1,NVAR
          YSTART(I)=Y(I)
14      CONTINUE
          IF(KMAX.NE.0)THEN
            KOUNT=KOUNT+1
            XP(KOUNT)=X
            DO 15 I=1,NVAR
              YP(I,KOUNT)=Y(I)
15          CONTINUE
            ENDIF
          RETURN
        ENDIF
        IF(ABS(HNEXT).LT.HMIN) PAUSE 'Stepsize smaller than minimum.'
        H=HNEXT
16      CONTINUE
        PAUSE 'Too many steps.'
        RETURN
      END
C*****
C*****
      SUBROUTINE RKQC(Y,DYDX,N,X,HTRY,EPS,YSCAL,HDID,HNEXT,DERIVS)
      PARAMETER (NMAX=10,FCOR=.0666666667,
        * ONE=1.,SAFETY=0.9,ERRCON=6.E-4)
      EXTERNAL DERIVS
      DIMENSION Y(N),DYDX(N),YSCAL(N),YTEMP(NMAX),YSAV(NMAX),DYSAV(NMAX)
      PGROW=-0.20
      PSHRNK=-0.25
      XSAV=X
      DO 11 I=1,N
        YSAV(I)=Y(I)
        DYSAV(I)=DYDX(I)
11      CONTINUE
      H=HTRY
1      HH=0.5*H

```

```

CALL RK4(YSAV,DYSAV,N,XSAV,HH,YTEMP,DERIVS)
X=XSAV+HH
CALL DERIVS(X,YTEMP,DYDX)
CALL RK4(YTEMP,DYDX,N,X,HH,Y,DERIVS)
X=XSAV+H
IF(X.EQ.XSAV)PAUSE 'Stepsize not significant in RKQC.'
CALL RK4(YSAV,DYSAV,N,XSAV,H,YTEMP,DERIVS)
ERRMAX=0.
DO 12 I=1,N
  YTEMP(I)=Y(I)-YTEMP(I)
  ERRMAX=MAX(ERRMAX,ABS(YTEMP(I)/YSCAL(I)))
12 CONTINUE
ERRMAX=ERRMAX/EPS
IF(ERRMAX.GT.ONE) THEN
  H=SAFETY*H*(ERRMAX**PSHRNK)
  GOTO 1
ELSE
  HDID=H
  IF(ERRMAX.GT.ERRCON)THEN
    HNEXT=SAFETY*H*(ERRMAX**PGROW)
  ELSE
    HNEXT=4.*H
  ENDIF
ENDIF
DO 13 I=1,N
  Y(I)=Y(I)+YTEMP(I)*FCOR
13 CONTINUE
RETURN
END
C*****
C*****
      FUNCTION ACTY(X)
      COMMON/SAI/ALPHA
      PARA1=2.0*(3.0-ALPHA)
      PARA2=(4.0/3.0)**(3.0-ALPHA)
      PARA3=(4.0/3.0)**(3.0+ALPHA)
      IF(X.LE.0.725) GO TO 20
      GO TO 30
20    ACTY=(19.0/192.0)*(3.0-ALPHA)*PARA1*PARA2*(X**(-ALPHA))
      1 / (PARA1-PARA2)
      GO TO 40
30    ACTY=(37.0/192.0)*(3.0+ALPHA)*PARA3*(X**ALPHA)/(PARA3-1.0)
40    RETURN
      END

```